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LUBRICATION WITH NATURALLY OCCURRING DOUBLE OXIDE FILMS

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A study was conducted to evaluate the lubricating characteristics of double oxides which could occur naturally on high temperature bearing materials. Consideration was given to the double oxides of iron, nickel, cobalt, rhenium, osmium, molybdenum, tungsten, vanadium, chromium, copper, titanium, aluminum, boron, and niobium. A survey was conducted to obtain property data on such compounds and a number selected for evaluation. Primary

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) consideration was given to the rhenates, molybdates, vanadates, borates, osmoniates, and chromates. Friction tests were run over the temperature range 26 to 650C with single oxides, double oxides, and metal powders which would form such oxides. Results showed that the oxides which had the greatest potential for spanning the required temperature range were the copper and cobalt rhenates, borates, and molybdates. Sliding friction coefficients for copper rhenate vary from 0.35 at 400C to 0.14 at 600C. Additions of copper and rhenium to a cobalt base alloy lowered friction values to 0.21 over the temperature range 200 to 650C. Theoretical considerations of the wear of surface films suggest that there is an optimum hardness and bearing design for maximum life. To achieve the cruise missile engine bearing requirements, film wear coefficients of 10^{-7} to 10^{-8} will be requirements. Preliminary rolling ball and rolling contact bearing tests with plasma sprayed coatings containing oxidizing additives did not achieve such wear coefficients due to coating breakup in the contact area. Further testing is recommended with cast alloys and ion implanted surfaces.

SUMMARY

A study was conducted to evaluate the lubricating characteristics of double oxides which could occur naturally on high temperature bearing materials. The purpose of the program was to evaluate the feasibility of lubricating rolling contact bearings over a wide temperature range using the naturally occurring oxide films. Consideration was given to the double oxides of iron, nickel, cobalt, rhenium, osmium, molybdenum, tungsten, vanadium, chromium, titanium, aluminum, boron and niobium since these are the metals commonly used in high temperature alloys.

As a first step in the program a survey was conducted to obtain property data on such compounds. Data collected included primarily melting point, hardness, structure and high temperature stability. Friction coefficients were also obtained using each of the oxides of the above metals as lubricants over the temperature range 200 to 650C. Based upon these friction coefficients and double oxide properties the following compounds were chosen for evaluation: rhenates, osmoniates, molybdates, vanadates, borates, and chromates. Sliding friction tests were run on mixed metal oxides which could produce the desired double oxide as well as the double oxide itself over the desired temperature range. The best results were obtained with copper and cobalt rhenates, borates and molybdates. At 600C, the following friction coefficients were obtained: Copper rhenate - 0.14; Copper borate - 0.16; Rhenium borate - 0.17; Cobalt oxide - 0.18; Cobalt borate - 0.18; Cobalt rhenate - 0.20; Copper oxide - 0.22; Copper molybdate - 0.23; rhenium oxide - 0.24; Cobalt molybdate - 0.28. When both high temperature and low temperature are considered, the best results, considering both friction and surface damage, were obtained with copper rhenate, copper molybdate and cobalt borate.

In order to determine if such compounds could be produced and would effectively lubricate the alloys on which they were formed, a number of sliding and rolling tests were conducted on mixed metal powders and certain alloys which contained the lubricant producing metals. Results on the metals were compared with that for the oxide alone. The best results were obtained with metals powder mixtures of copper/rhenium, copper/molybdenum, and cobalt/molybdenum. Similar results were obtained with solid alloys of rhenium and rhenium/molybdenum. Plasma sprayed coatings were prepared using a cobalt alloy base with additions of copper, rhenium and molybdenum. Without the additions, friction coefficients ranged from 50 at room temperature to 0.32 at 600C. With the additions, the friction co icient is approximately 0.23 over the temperature range.

Based upon these results, three lubrication concepts were proposed for oxide lubrication over a broad temperature range:

(1) The natural occurring oxide on the <u>bearing metal</u> provides effective lubrication at high temperatures. This oxide also gives adequate protection at low temperatures.

(2) The natural occurring oxide on a <u>carbide or boride</u> surface (bonded solid or film) provides effective lubrication at high temperatures. The <u>carbide or boride itself</u> gives adequate protection at low temperatures.

(3) Use either (1) or (2) as a race material combined with a low temperature lubricant (silver or cobalt) coated on the ball.

Theoretical and experimental studies were initiated to evaluate these concepts. Theoretical considerations of the wear of surface films in a rolling contact suggests that wear can occur by plastic flow, adhesion, or fracture. If this is true there will be an optimum film hardness and optimum bearing parameters to achieve maximum life. Required wear coefficients were determined for a typical turbine engine bearing to achieve 25 hours life. It was found that $K^*=10^{-7}$ to 10^{-8}; this is much lower than that usually found for the wear rate of solid surface films and lower than that found for bearing tests run to date on plasma sprayed films containing lubricants.

Full complement GT-7 ball thrust bearings were run using the above lubricant concepts. Bearing tests were run for several hours at 430C using plasma sprayed coatings containing a cobalt base alloy with metal powder additions of copper, rhenium, and molybdenum. Even though effective films appeared to be formed, wear rates were high due to the breakup of the films.

PREFACE

This work was performed under Contract N00014-82-C-0247 with David K. Beck as contracting officer under DARPA Order 4477. The program manager was Dr. Robert E. Green, Jr. from the Defense Science Office of the Defense Advanced Research Projects Agency. Bearing tests were run at Georgia Tech by Scott Bair and Dr. Ward Winer. Bearings for the tests were supplied by M. Gardos through the DARPA Solid Lubrication Program. Their contributions are acknowledged with gratitued. M.B. Peterson acted as project manager. The testing was carried out at RPI's Tribology Laboratory under the direction of S. Calabrese. B. Stupp, President of Hohman Plating and Manufacturing, applied the surface films. Dr. E.F. Finkin contributed the theoretical evaluation.

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INTRODUCTION

Since 1950 a considerable amount of effort has been devoted to the lubrication of rolling element bearings with solids. Almost every conceivable approach has been suggested and evaluated at one time or another. This includes films (1) (2) (3); reservoirs placed in the cage and lands (4); composite cages which supplied lubricant by rubbing against the balls (5) (6) (7) (8); alternative balls or metal and lubricant composite; lubricant composite balls and races (9), replacing the cage with spring loaded sticks(10) to rub against the ball; vapor lubrication with reactive gases (11) (12) either sprayed into the bearing or self contained; powders blown into the bearing (13) and finally, a self-contained recirculation system for powders (14). More recent research into ceramic rolling contact bearings (SiN and Al_2O_3) and the effectiveness of hard coatings for tribological applications have renewed interest in this approach. Because of this, a major program (DARPA/AFWAL/HUGHES Solid Lubricated Rolling Element Bearing Program) was initiated to establish the feasibility of advanced dry-lubricated bearings (15) (16) (17) (18) (19). The ultimate goal of this program is the development of a hi-temperature solid lubricated turbine engine bearing to replace the temperature limited fluid lubricated systems currently in use.

The main problem in lubrication over a broad temperature range is illustrated in Figure 1. If low temperature lubricants are used they are destroyed at high temperatures; if high temperature lubricants are used they are ineffective at low temperatures. Thus, improved lubricants or lubricating techniques are required which will allow a broad temperature operating range. One technique that merits investigation is the use of the naturally occuring oxide as the primary lubricant and adjusting its composition so that it is effective over the desired temperature range for a rolling contact.

Oxides are effective lubricants and have been shown to prevent damage of certain high temperature alloys with both sliding and rolling contacts. They have the advantage of not requiring an additional supply system and since they build up on the surface, they compensate to some degree for film wear. The disadvantages, however, are that they are primarily high temperature lubricants (<400C) and techniques must be devised to insure proper operation at low temperatures. There are several ways of doing this:

(1) Develop oxide lubricants which are effective in themselves for rolling contacts over a broad temperature range.

(2) Combine a high temperature oxide lubricant with a low temperature lubricant (such as graphite or silver) which will be effective during continuous temperature cycling.

(3) Choose materials which will operate unlubricated, without failure, during temperature cycling but are lubricated with the naturally occuring oxide at high temperature.

The object of this study is to explore the concept of the lubrication of rolling contacts with the naturally occuring oxide with particular emphasis on broad temperature range operation.

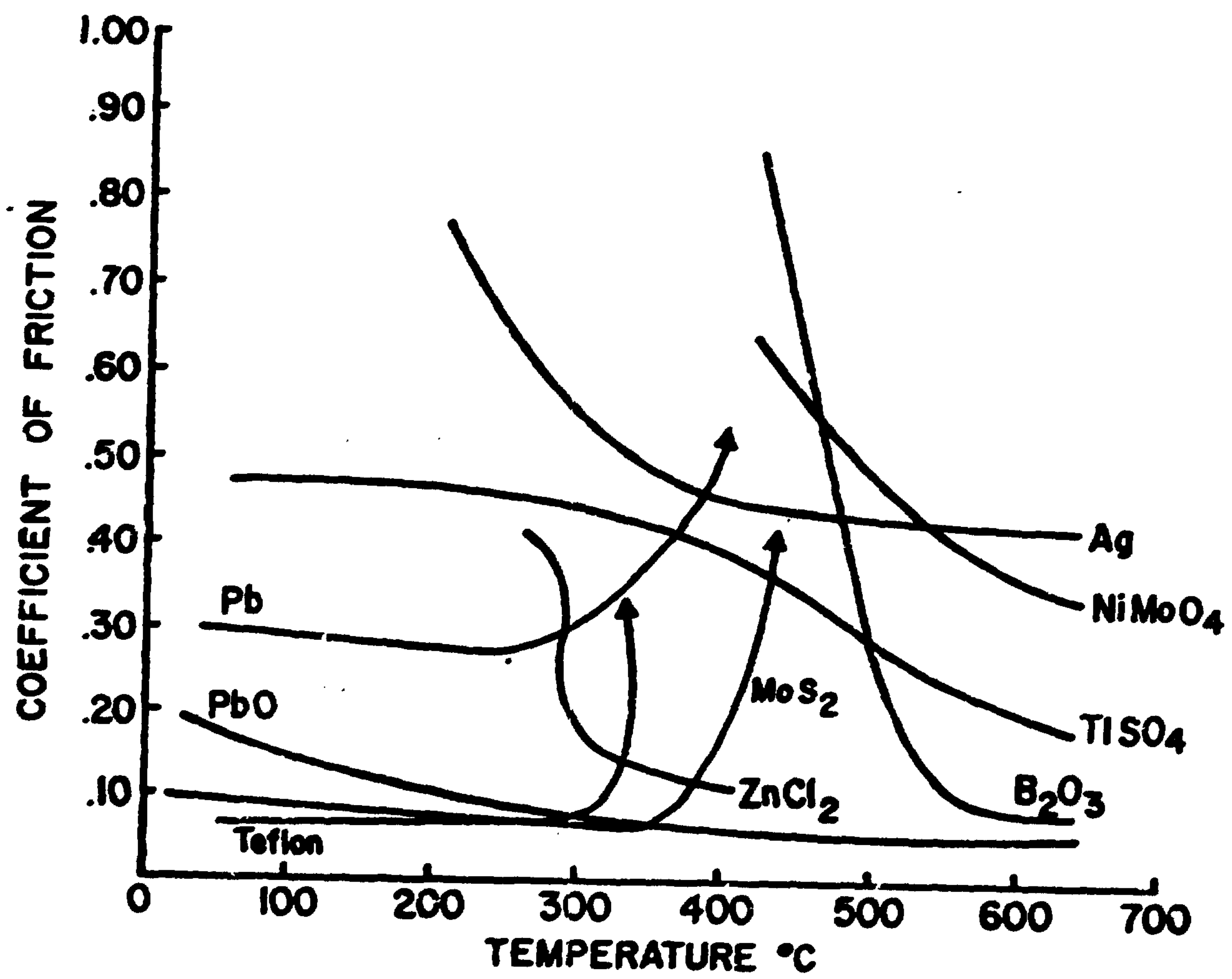

Fig. 1 Friction coefficients for a variety of solid materials vs temperature (29).

BACKGROUND

The role of surface reaction films in preventing damage to sliding contacts is well established. Chlorine and sulfur containing compounds have been used in lubricants for many years. The search for solid lubricants has isolated numerous compounds such as MoS_2, CdI_2, $NiCl_2$, $CoCl_2$ (20), which have varying degrees of lubricating capacity. It has also been demonstrated that effective sliding will result if such films are formed by reaction of the metals with the environment, for example, the lubrication of steel, nickel and cobalt with chlorine and bromine substituted methane gases (21) and the effective sliding of molybdenum in H_2S gases (22)

In recent programs the search for solid lubricants has continued for the temperature range of 700-1000F,(23) and 1000-1500 (24). These studies have indicated that there are many oxide films which are soft enough to prevent surface damage when applied as powders to sliding contacts of inconel. A list of friction coefficients at 1300F for three classes of oxides are given below:

Single Oxides		Molybdates		Tungstates	
PbO	.12	$PbMoO_4$	.29	$PbWoO_4$	.35
MoO_3	.20	$NiMoO_4$	.29	$CuWoO_4$	.41
Co_2O_3	.29	$AgMoO_4$	.28	$FeWoO_4$	.49
CuO	.45	$FeMoO_4$	.42	$NiWoO_4$	.51
ZnO	.33	$AgMoO_4$	.28		
WO_3	.55	K_2MoO_4	.20		
B_2O_3	.10				

These oxides, however, are not effective lubricants at room temperature.

The mechanism of lubrication is not entirely clear. It is known that B_2O_3 behaves as a viscous film, since from the friction data one can obtain its activation energy of viscous flow. Whether the other oxides behaved in a similar manner has not been determined. For the molybdates and the tungstates the friction coefficient was proportional to the difference between test temperature and melting temperature.

In separate programs (25) in which the sliding behavior of materials was investigated, it was found that those materials performed best which could form these films. For example, the most effective materials found for high temperature sliding were cobalt base alloys, tool steels which contained molybdenum and cobalt, S monel which contains copper, and alloys such as the Hastelloys which contained appreciable amounts of molybdenum. Further evidence also indicated that even the presence of small amounts of molybdenum improved the sliding behavior of nickel base alloys and nickel bonded cermets. Although the films were not identified, it is known that molybdate films are formed on certain alloys by high temperature oxidation.

Work by other investigators has also given similar results. Battelle (26) has found that molybdenum and tungsten are effective sliding materials for sodium and NaK. This has been attributed to the formation of sodium molybdate and tungstate at the sliding interface. Here the films were identified. McDonald (27) showed that the presence of cobalt and molybdenum in certain percentages in steel gave improved friction, wear and surface damage. In sliding tests in steam environments (28) the best sliding behavior was found with those materials which formed soft oxide films.

Thus the evidence seems clear that effective material combinations may be selected by choosing those materials which by reaction with the environment of each other form easily sheared, mixed oxide films. However, at the present time this approach is limited because information on the frictional behavior of the mixed oxides is limited to the molybdates and the tungstates. There are many other mixed oxides which may give similar results. Secondly, the data which does exist does not span a broad temperature range or apply necessarily to rolling contacts. To provide such information the present study was conducted. It consists of the selection and evaluation of double oxides which might be formed on specially fabricated high temperature alloys. Techniques are then considered for their utilization in temperature cycling rolling contact bearings. Finally, some representative rolling contact bearings representing these concepts were run at various temperature levels.

APPARATUS AND PROCEDURE

For this investigation the test rigs shown in Figures 2 and 3 were used. The reciprocating arm was used for both sliding and rolling tests; thrust bearings were evaluated in the bearing tester.

The reciprocating arm consists of a pin sliding back and forth on a flat plate. It was also used as a rolling test with a ball rolling back and forth on a flat plate. The pin is held in an arm which is moved back and forth at one end by an air cylinder. Strain gages mounted between the cylinder and the arm allow friction force to be measured. The other end of the arm is mounted in ball bearings so that it is free to move in any direction with minimum friction. The load in these experiments is 142N (32 lbs) which is the weight of the arm measured at the pin. The pin moves back and forth over a single track 2.5 cn (1 in) in length at a rate of 2.5 cn/sec.

A furnace surrounds each specimen so that tests can be run at any temperature level up to 900C (1650F). Most of the tests reported herein were conducted at 600C (1112F); however, a limited number of tests were conducted at lower temperature levels.

With the reciprocating tester, the test procedure was as follows: The specimens were cleaned and placed in the apparatus. The furnace was brought to the desired operating temperature and allowed to stabilize. The arm was then raised and powder placed on the surface of the flat to a depth of approximately .3 cn (0.125 in). The load was then reapplied, the test started and run, usually for a period of 5 minutes. Friction and friction variation was recorded and monitored throughout the test. At the conclusion of the test the specimens were examined microscopically for wear, surface damage, film formation and chemical corrosion or interactions. The data presented was usually the friction coefficient; initial and final.

The bearing tests were run on the Georgia Institute of Technology thrust bearing test. Essentially, this consists of a GT-7 cageless ball thrust bearing mounted

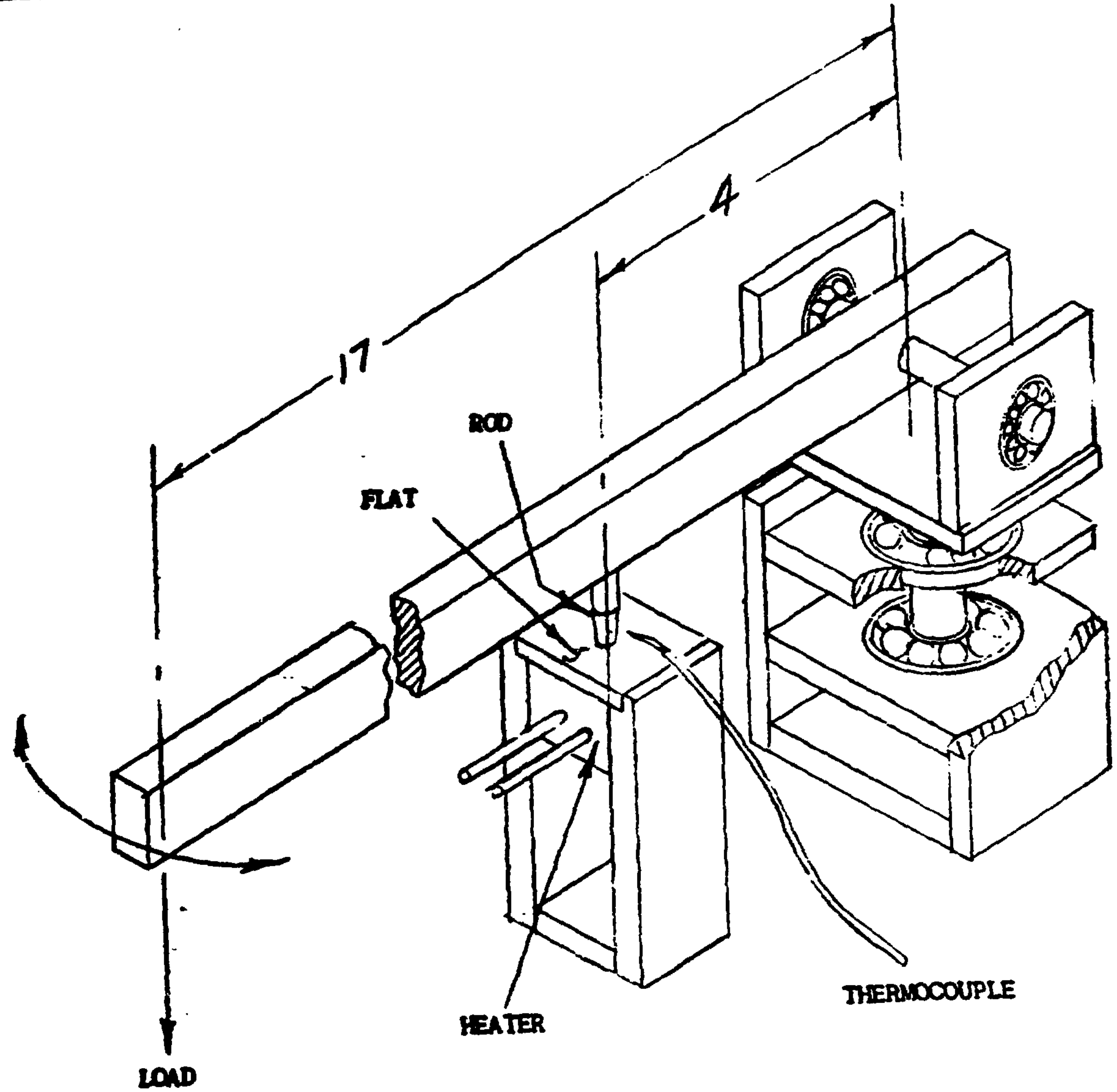

FIGURE 2
SCHEMATIC DIAGRAM OF WEAR APPARATUS

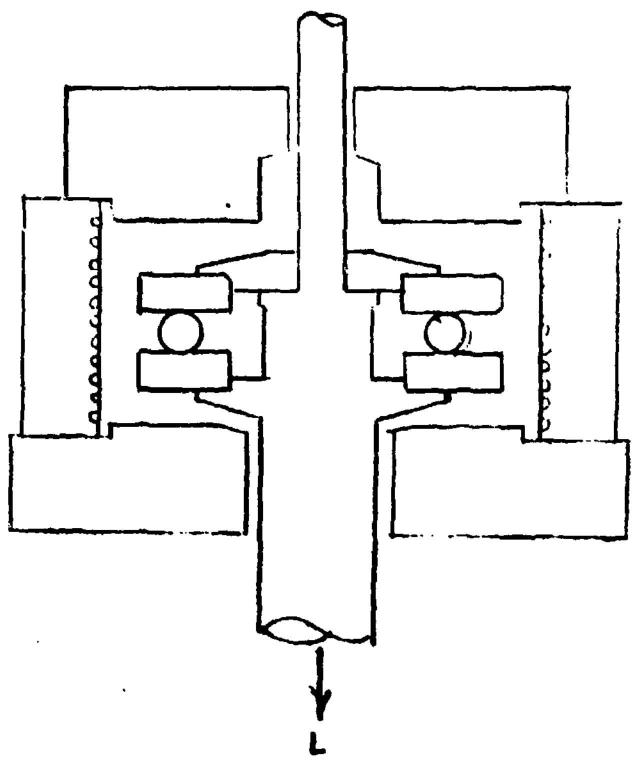

Figure 3. Schematic of Thrust Bearing Test Rig

on a variable speed spindle. A furnace surrounding the bearing allows the temperature to be set at any desired level up to 430C (806F). Air pressure is used to load the bearing. The tests were run at a velocity of 300 RPM at a load of 116N (26 lbs) which amounts to a ball/race pressure of 124 x 10^6 Pa (180,000 psi). Stack height was measured before and after the test as an indication of wear. The surfaces were also examined microscopically for evidence of damage or film formation.

In the bearing test the following procedure was used: The bearing was cleaned and mounted in the apparatus. It was lubricated with several drops of cetane and run at room temperature for a period of 1 hour at a load of 35.6N (8 lbs). The bearing was then disassembled, cleaned and installed in the test rig. The temperature was increased to 400C and the test run for 1 hour at a load of 116N (26 lbs). The wear (stack height) was measured before and after each run. The bearing condition was monitored by vibration and noise during the course of the test.

RESULTS

SELECTION OF OXIDE MATERIALS

Two main criteria were used in the selection of oxide lubricating materials. First, since the alloy must oxidize to produce the lubricant, the added metal must be compatible with high temperature alloys. This means that certain low melting point metals such as lead, bismuth, antimony, etc., cannot be used since they would seriously reduce the strength of the alloy. Unfortunately, these are the metals which would produce oxides with known lubricating effectiveness. The second criterion is that of hardness. Although solid lubricant technology has advanced the understanding far beyond this point, the choice is so limited that no potential compounds should be eliminated in a feasibility study. These two criteria can be considered by referring to Table 1. In the left hand column are listed those metals which could be added to high temperature alloys. Their stable oxides, melting points, and hardness are also shown. Lubricating double oxides would necessarily consist of some mixture of these oxides. To identify such compounds a literature search was conducted to identify stable compounds of each of the oxides listed in Table 1. Unfortunately, hardness of such compounds is rarely specified. Therefore, another technique was used. From data on hardness and melting points of oxides (and other materials) the graph shown in Figure 4 was constructed. It is known that in a general way hardness and melting point are related. It has also been shown that the friction coefficient is proportional to melting point (29). From Figure 4 it can be seen that effective lubricating oxides (PbO, $PbMoO_4$, Cdo, and Sb_2O_3) as reported in the literature, have melting points in the range 800 to 1200C. Thus, double oxides with similar melting points should be considered. A listing of such compounds using only Table 1 elements is given in Table 2. Hardness data predicted from Figure 4 is also shown. Examination of this table indicates the potential of the following:

Rhenates
Molybdates
Vanadates
Borates

These compounds have low melting points and hardness because of the presence of one low melting point ingredient (Re_2O_7, MoO_3, V_2O_5, or B_2O_3). Thus, similar results would be expected from OsO_4 and CrO_3.

Rhenium is a high temperature material like molybdenum and tungsten. It has a hexagonal crystal structure with a melting point of 3167C. It is stable in air to 300C, the oxidation becoming rapid above 600C. Alloys of rhenium have been prepared with most high temperature materials such as iron, nickel, and cobalt forming solid solutions with increased strength. Rhenium-molybdenum and rhenium-tungsten alloys are commercially available substitutes for molybdenum and tungsten, but with improved ductility and workability. Thus, it is a practical additive for high temperature bearing materials.

Molybdenum is an ingredient in many high temperature alloys and in tool steels, which are limited to temperatures below 500C. In fact, the effective sliding and rolling behavior of tool steels is probably due to the formation of molybdates films. Chromium is also a common ingredient of high temperature alloys,

TABLE 1

OXIDE REFERENCE DATA

Metal	Oxide	Melting Point °C	MoH Hardness	Remarks
Fe	FeO	1641	5	
	Fe_3O_4	1831	5.5	
	Fe_2O_3	1835	6	
Ni	NiO	2230	5	
Co	CoO	2078	(5.5) *	
	Co_2O_3	1168	(4)	
Re	Re_2O_7	296	(1)	Layer Lattice
	ReO_2	1200	(4)	
Os	OsO_4	130	2	Poison
Mo	MoO_3	795	1.5	Layer Lattice(Glass)
W	WoO_3	1473	5	(Glass)
V	V_2O_5	670	(3)	Toxic (Glass)
	V_2O_3	1977	8.5	Toxic
Cr	CrO_3	460		
	Cr_2O_3	2573	8.5	
Cu	Cu_2O	1229	4	
	CuO	1336	3.4	
Ti	TiO_2	1855	5.5	
AL	AL_2O_3	2047	9	
B	B_2O_3	450	-	Glass Former
Nb	Nb_2O_5	1460	(4.5)	
	NbO	2377	(6.5)	

( )*From Figure 4

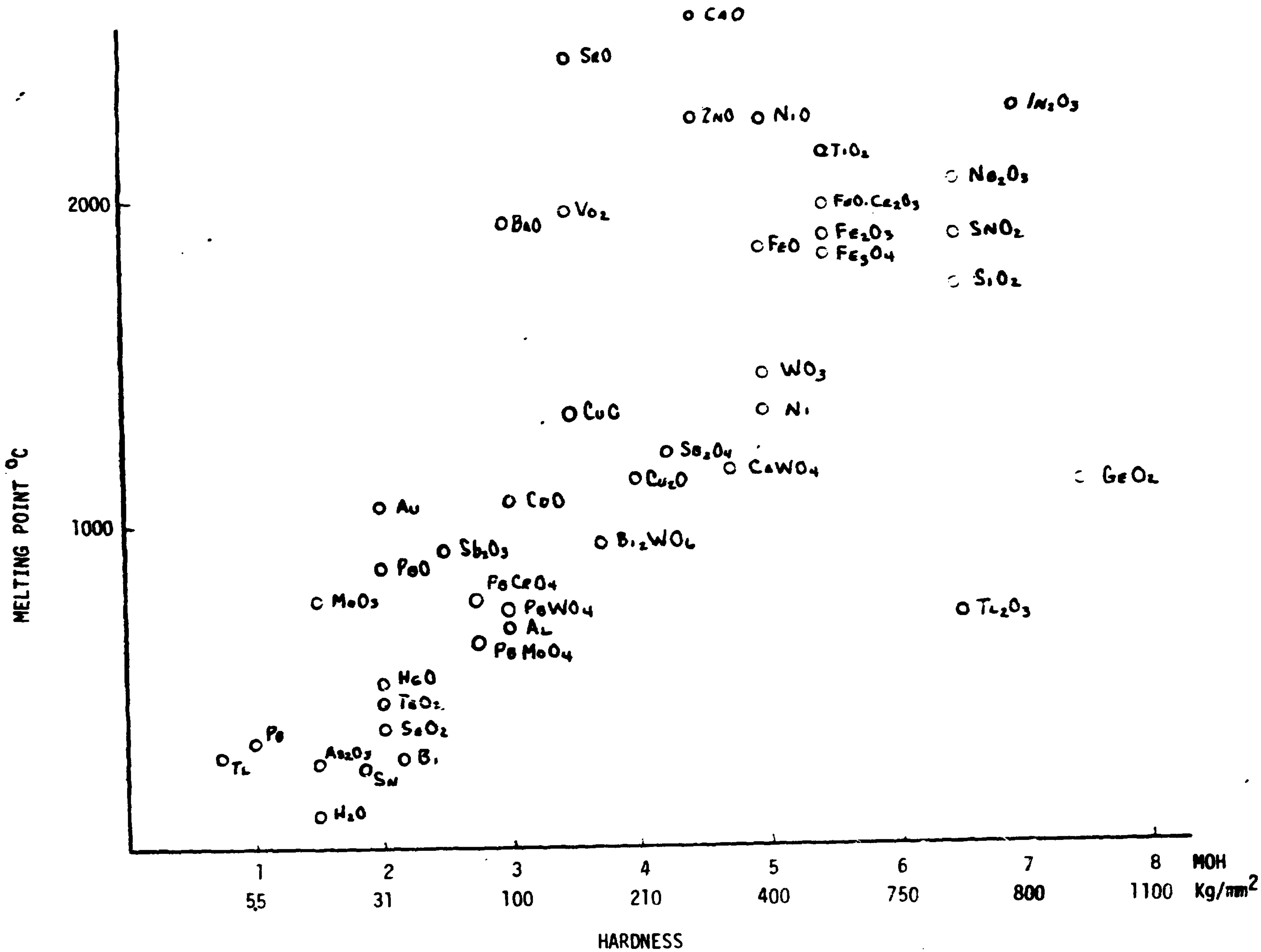

Figure 4. Melting Point/Hardness Correlation for Oxides

TABLE 2

MELTING POINTS OF DOUBLE OXIDES

Compound	Melting Point °C	Moh Hardness*
$Cu_2(ReO_4)_2$	380	1.5
$CuMoO_4.MoO_3$	560	2
$MoO_3.V_2O_5$	618	2
$Nb_2O_5.V_2O_5$	648	2.5
$Cr_2O_3.V_2O_5$	650	2.5
$Al_2O_3.V_2O_5$	658	2.5
$V_2O_3.WO_3$	660	2.5
$FeMoO_4.MoO_3$	705	2.5
$CuV_2O_5.V_2O_5$	711	3
$Co(ReO_4)_2$	816	3
$CuO.B_2O_3$	900	3
$Cr_2O_3.FeO$	900	3
$CuO.WO_3$	930	3.5
$CuO.Fe_2O_3$	1070	3.5
$NiO.MoO_3$	1090	4.0
$CuO.Al_2O_3$	1131	4.0
$2CoO.B_2O_3$	1150	4.0
$Al_2O_3.WO_3$	1190	4.0

*From Figure 4

however, it is unlikely that chromates would be produced as a result of its oxidation; more likely chromites (MeO. Cr_2O_3). Vanadium and boron are used in small amounts for hardening without serious detrimental effects. Thus, each of the above metals are practical for inclusion in high temperature rolling contact bearing materials. Osmium is a very hard wear resistant metal (30). However, as noted in Table 1, its oxide is poisonous, therefore it was not given further consideration.

For completeness, compounds (rhenates, molybdates, vanadates, borates, chromates) containing each of the anions listed in Table 1 should be considered as potential lubricating oxides. However, to demonstrate feasibility, only several need be selected. Iron, nickel, and cobalt would be the most practical since they would be present in the largest quantities in common high temperature materials; however, the other metals are not impractical. In order to make an appropriate selection it was decided to choose those metals which in themselves yielded some degree of lubricating effectiveness over the desired operating range (26-650C). This evaluation of single oxides was conducted as the first step in the selection of the most effective double oxide for lubrication over a broad temperature range.

LUBRICATING BEHAVIOR OF SINGLE OXIDES

In order to select the most appropriate double oxides a series of screening tests were conducted on the single oxides over a wide temperature range. Friction coefficients were obtained at three temperature levels for annealed tool steel pin (1" radius) sliding against sand blasted 304 stainless steel flat. The flat was covered with the oxide powder to a depth of 0.5 cm. The results are shown in Table 3. Data were obtained on all the oxides listed in Table 1; PbO and the unlubricated condition are shown for comparison purposes. Based upon these friction coefficients and an examination of the surfaces at the conclusion of the tests the following conclusions can be drawn: At 200C, CrO_3 and Re_2O_7 are effective lubricants; however, at higher temperatures the Re_2O_7 vaporizes while the CrO_3 reacts with the surface and oxygen. By themselves they could not be used above 200C. At approximately 600C many oxides were effective lubricants, the most effective being B_2O_3, ReO_2, CuO, Cu_2O, CoO, MoO_3, Fe_3O_4 and V_2O_5. Considering both low and high temperatures, leads to the selection of CoO, CuO, V_2O_5, and Fe_3O_4. These oxides formed sheared films on the surface even at 200C and prevented surface damage even though they gave high friction at the lowest temperature. Thus, based upon these results, primary consideration was given to Cu and Co chromates, rhenates, borates, molybdates, vanadates, and oxides as naturally occurring rolling contact lubricants.

LUBRICATING BEHAVIOR OF DOUBLE OXIDES

Potential double oxides were selected based upon the results of the previous sections. These were evaluated in tests similar to that for the single oxides, with primary emphasis on copper and cobalt compounds. For these tests a 3 to 1 weigh percentage of CuO or CoO was used. This mixture is arbitrary and does not represent a stoichiometric compound. Stoichiometric compounds must be mixed in certain proportions which would be different for each compound tested. Furthermore, there is no reason to believe that such compounds would be found uniquely in the naturally occurring oxide or be formed under sliding conditions. Basically, the naturally occurring oxide is a mixture in various proportions which is subjected to the compressive and shearing stresses at high interface temperatures. It was felt that the mixture of oxides more simulated actual processes

TABLE 3

SLIDING FRICTION COEFFICIENTS FOR SINGLE OXIDES

T15 Tool Steel vs Sand Blasted Stainless

	400F(204C)	600F(316C)	1100F(593C)
Unlubricated	.78* - .46**	.75	.60 - .80
PbO	.19**	.10	.10
B_2O_3	.64	.51	.18
CrO_3	.14	X	X
Re_2O_7	.35	.23	X
ReO_2	.64	-	.27
Cu_2O	.30	.14	.48
CuO	.60	.50	.23
CuO	.46	.38	.18
MoO_3	.51	.69	.38
WoO_3	.41	.60	.56
Fe_3O_4	.60	-	.40
Fe_2O_3	.46	-	.42
V_2O_5	.53	.52	.32
TiO_2	.68	-	-
AL_2O_3	.77	-	-
Cr_2O_3	.41	.64	-
NiO	.70	-	.69

* Initial friction coefficient

** Friction coefficient after 5 minutes

than pure compounds.

The data obtained on the selected oxides is given in Table 4 which shows the friction coefficient after five minutes of sliding at both 200C and 600C. The evaluation also included a microscopic examination of the surfaces at the conclusion of the test which considered the nature of the film and the metal surface damage.

The best results were obtained with copper rhenate (a 3 to 1 mixture of CuO and Re_2O_7). Polished films were formed at both temperature levels with little or no surface damage. Low friction was also found at high temperatures. The friction coefficient of 0.14 was the maximum value; the initial friction coefficient was 0.09. A similar series of tests were run with $Cu_2O.Re_2O_7$; it gave friction coefficients of 0.32 at both 200C and 600C. It was not considered further because of the high friction at high temperatures. Copper molybdates gave similar results and it was difficult to differentiate between them except for small differences in friction. A purchased copper molybdate gave similar results but with slightly higher friction. Cobalt compounds were also effective but gave higher friction at lower temperatures than the CoO by itself; the films of mixed oxides however appeared more complete and continuous.

The lubricating properties of B_2O_3 are well known. Data obtained under the present test conditions are as follows:

Temp ^oC	Friction Coefficient
650 (1200F)	.09
593 (1100F)	.18
538 (1000F)	.28
482 (900F)	.68
427 (800F)	1.50
204 (400F)	.64

B_2O_3 is a liquid glass at 650C and is as effective a lubricant at those temperatures as oils at lower temperatures. Unfortunately the glass solidifies at 425C yielding high friction (1.50). Below this temperature the film is brittle and would be spalled from the surface in either a sliding or rolling contact. Because of this, a great deal of effort was devoted to boric oxide mixtures and compounds. Essentially, what is needed is some way to promote compound formation rather than glass formation. As a preliminary approach to this problem, 3/1 mixtures of all the oxides listed in Table 1 were prepared and evaluated. In no case was the high friction producing glass formation avoided. Although the CuO and CoO gave better film formation and lower friction at 200C, high friction still persisted at 425C. The only exception to this behavior was rhenium. Rhenium oxide/boric oxide mixtures gave the high friction peak upon cooling; however, when allowed to stand several hours at room temperature, they absorbed water. Upon heating, the high friction was avoided. This may be a solution in isolated cases, but

TABLE 4

FRICTION COEFFICIENTS FOR DOUBLE OXIDES

	Chromates		Rhenates		Borates		Molybdates		Vanadates		Oxides	
	200C	600C	200C	600C	200C	600C	200C	600C	200C	600C	200C	600C
Copper												
Mixture	.46	.43	.37	.14	.55	.16	.41	.23	-	-	.60	.22
Compound	-	-	-	-	-	-	.59	.28	.34	.37		
Cobalt												
Mixture	.20	.41	.60	.20	.46	.18	.69	.28	-	-	.46	.18
Compound	-	-	-	-	-	-	.37	.37	-	-		
Molybdenum												
Mixture	-	-	.64	.46	-	-			-	-	.51	.38
Compound	-	-	-	-	-	-			-	-	-	-
Rhenium												
Mixture	-	-	-	-	.46	.17	-	-	-	-	.35	.24
Compound	-	-	-	-	-	-	-	-	-	-	-	-

impractical for most. Much more effort is needed to develop effective borate compounds. The borate compounds shown in Table 4 are the ones which could be considered if only high temperature and low temperature operation were required.

Other compounds tested (those listed in Table 4) and other blends did not prove to be as effective as copper and cobalt rhenates, molybdates and oxide.

The frictional behavior of the most effective compounds as a function of temperature is shown in Figure 5.

LUBRICATION WITH OXIDIZING METALS

Even though several of the compounds of Table 4 were shown to be effective lubricants as powders over a broad temperature range, their effectiveness as a naturally occurring oxide must also be demonstrated. First of all, such compounds may not be formed on alloys which contain the appropriate metal constituants either because the temperatures are inadequate or because the energetics are wrong. Secondly, even if it is formed its influence may be masked (or enhanced) by the presence of other oxides. The only way to be absolutely sure is to prepare alloys containing copper and rhenium and to evaluate them in sliding and rolling contacts. Preparing new alloys however is a costly and time consuming process and could not be undertaken until the consituants were well established and studies undertaken to determine interactive effects on other properties. Because of this, a different technique was used which consists of evaluating the sliding characteristics of a metal pin sliding against mixed metal powders. This technique and its development is described in the following paragraphs.

The approach used is illustrated in Figure 6. Essentially a pin is slid against a very rough surface. Mixed metals in the proportions which would constitute an alloy or additive are placed on the surface as powders and the frictional behavior determined. This appears to simulate the frictional process in an alloy. The metal asperities would act as the basic alloy structure or as harder phases in that structure since it would support the load. The powder acts as an ingredient which during sliding will be packed into the grooves and may or may not provide an effective lubricating oxide film on its surface.

To test this approach, tests were run with a variety of materials and roughness producing treatments (etching, sandblasting, and machining) of different hardness. It was found that the most consistant results were obtained with a hardened grooved surface as depicted in Figure 7. These were machined in the surface of T15 tool steel with a 60° tool. In the test, powder was placed on the surface in sufficient quantity to fill the grooves. Friction was determined by sliding a hardened T15 tool steel pin against this surface.

In order to evaluate this approach, friction of a variety of metal powders was determined and compared with that for tool steel sliding against solids composed of the same materials. These data are shown in Table 5. The similarity in friction coefficients is obvious from the data. However, it should be noted that with certain materials such as cobalt and cobalt alloy 6 the friction changed from that of cobalt to tool steel after five minutes sliding.

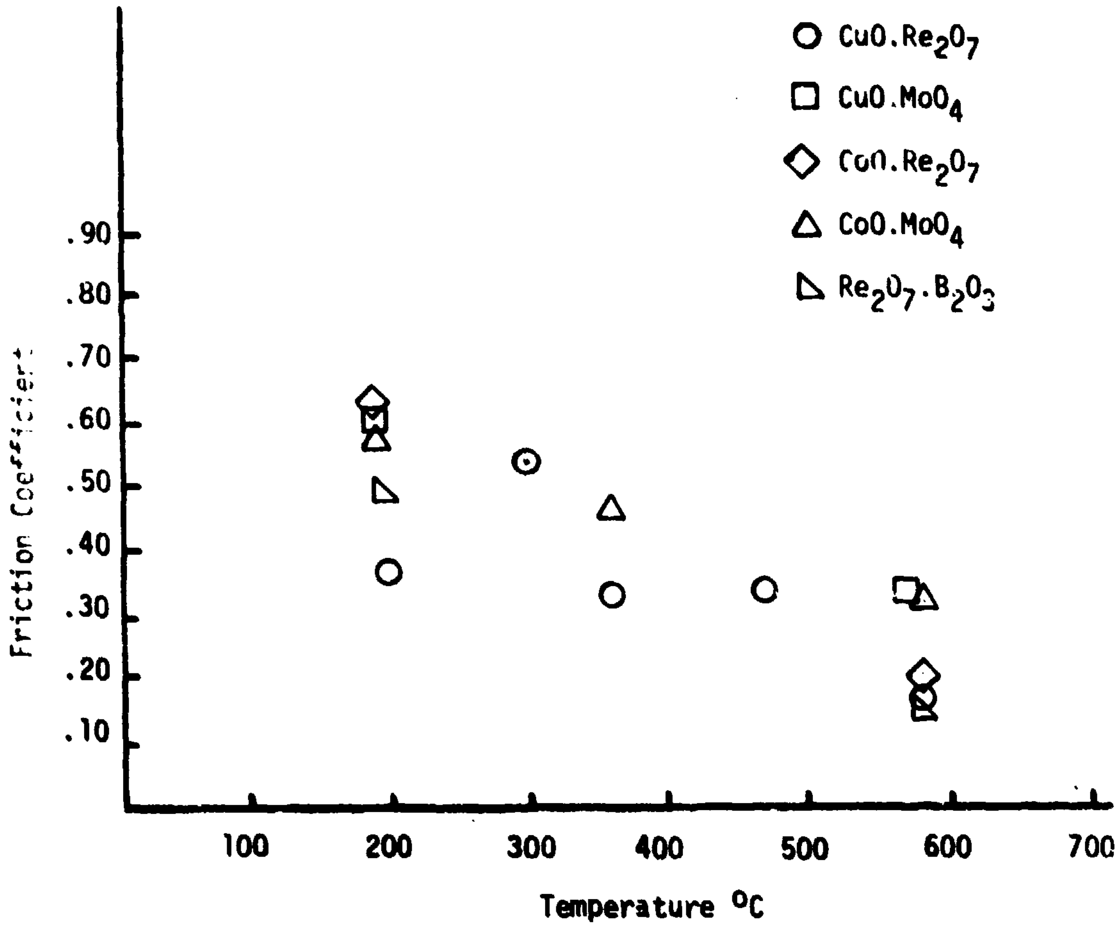

Figure 5. Effect of Temperature on the Coefficient of Friction for the Various Double Oxides.

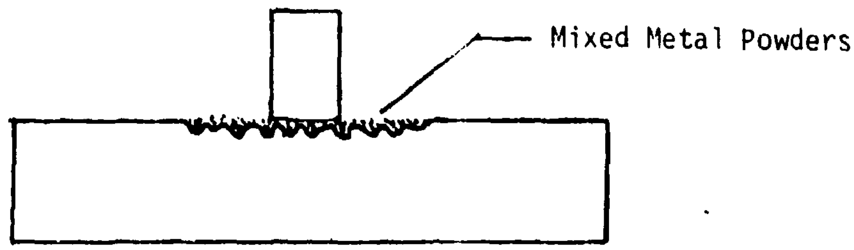

Figure 6. Diagram of Test Method for Mixed Metal Powders

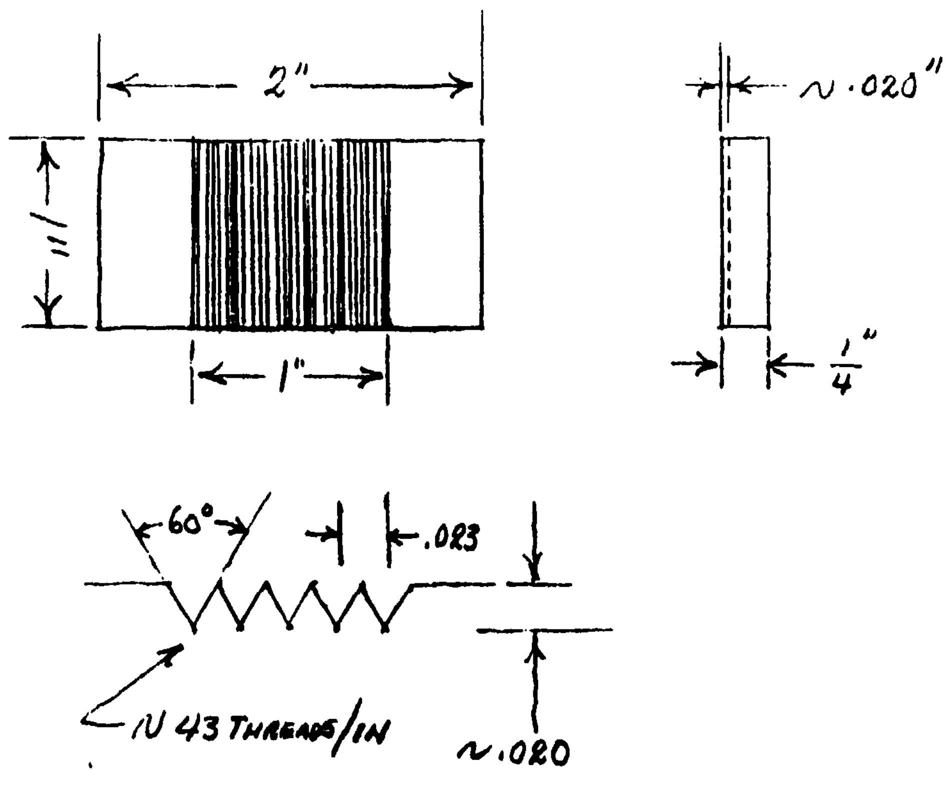

Figure 7. Diagram of Test Specimens for Evaluating Friction Properties of Mixed Metal Powders

TABLE 5

FRICTION WITH METAL POWDERS

Tool Steel vs Tool Steel (400F)

	Powders	Solid
Unfilled	-	.52
Mo	.70* - .80**	78 - .60
Co Alloy 6	.37	.36 - .53
Re	.39	.[illegible]1
B_4C	.41	--
B_4C+PbO	.20	.19***
Co	.46 - .52	.48

* Initial friction coefficient

** Friction coefficient after 5 minutes

*** Pbo as surface film

The most significant data however is that for B_4C to which 10 percent Pbo has been added. Under these circumstances friction is that for Pbo as a film. Thus it would be expected that if an oxide is produced by some combination of metals, its presence and relative lubricating effectiveness could be determined by this approach.

Using this approach a series of tests were run with metals, metal mixtures, and carbides which could produce the most effective oxides and double oxides of Table 4. These results are compared with those previously obtained for the desired oxide in Table 6. The materials chosen might be expected to form B_2O_3, Re_2O_7, CoO, CuO, Cu rhenate, cobalt rhenate, and Mo rhenate. The tests were run at 600C for a period of 5 minutes. Where mixed metals are used they were prepared using -325 mesh powder in 3 to 1 proportion.

From these data it can be seen that the most effective results were obtained with Co/Mo, Cu/Re, Re, and Cu/Mo although their friction coefficients are generally higher than that for the oxide alone. This might be expected if insufficient oxide was produced.

The boron containing compounds were rather unique. Those which oxidized sufficiently (eg. B, MoB, MoB_2, VB) gave high friction. Observation of the material behavior during and after the test indicated that when the oxide formed it was in the liquid state. This acted like an adhesive for the residual powder so that it behaved like a gummy mass; large areas were sheared rather than just that of a film on the surface. This is probably a case where the technique is not appropriate.

Using the metals which gave the best results a series of tests were run using this technique over a broad temperature range. These data are shown in Figures 8 to 12. Test conditions at each temperature were the same as those given for 600C tests.

The results for Cu/Re are shown in Figure 8, where its frictional behavior is compared with three oxides; CuO, CuO/Re_2O_7 and Re_2O_7 . It can be seen that Cu/Re behaves very similarly to CuO/Re_2O_7 above 320C. Below that temperature it behaves like CuO. As shown in Figure 9 the values for copper and rhenium are much lower at 200C so the oxide controls the frictional behavior at that temperature. CuO/Re_2O_7 generally falls somewhere in between CuO and Re_2O_7, favoring Re_2O_7 at the low temperatures.

The results for rhenium alone are shown in Figure 10 where rhenium metal powder is compared with Re_2O_7 powder, solid rhenium, and a solid molybdenum-rhenium alloy (~50% by weight rhenium). Re_2O_7 is an effective lubricant up to 320C where it vaporizes rapidly. The frictional behavior for the solid rhenium and the rhenium powder are essentially the same except that the powder oxidizes rapidly above 480C because of the small particle size. Oxidation and vaporization take place simultaneously. The molybdenum-rhenium alloy gives similar frictional trends to pure rhenium but with slightly higher friction. From these data it seems logical to propose that except for 480C region, the frictional behavior is controlled by the Re_2O_7. At that temperature the oxide vaporizes and is completely removed from the surface. Therefore, friction approaches that for the metal alone. At higher temperature studies (31) show that a film of liquid oxide forms on the surface from which vaporization takes place. This liquid oxide could be as effective as B_2O_3 is in liquid form if it has sufficient viscosity.

TABLE 6

POTENTIAL ALLOYS OR ALLOY CONSTITUANT

Oxidizing Metal Powder	f 600C	f Oxide
Co	.46	.18
Co/Mo	.27	.28
Cu/Re	.23	.14
Mo/Re	.41	.46
Co/Re	.41	.20
Re	.25	.28
Cu/Mo	.32	.23
Mo	.50	.38
Cu	.46	.48(Cu_2O)
B	.78	.18

Oxidizing Carbide Powder	f 600C	f B_2O_3
B_4C	.41	.18
MoB	.64	.18
MoB_2	.92	.18
VB	.92	.18
Co_2B	.46	.18
Re_2B	.55	.18

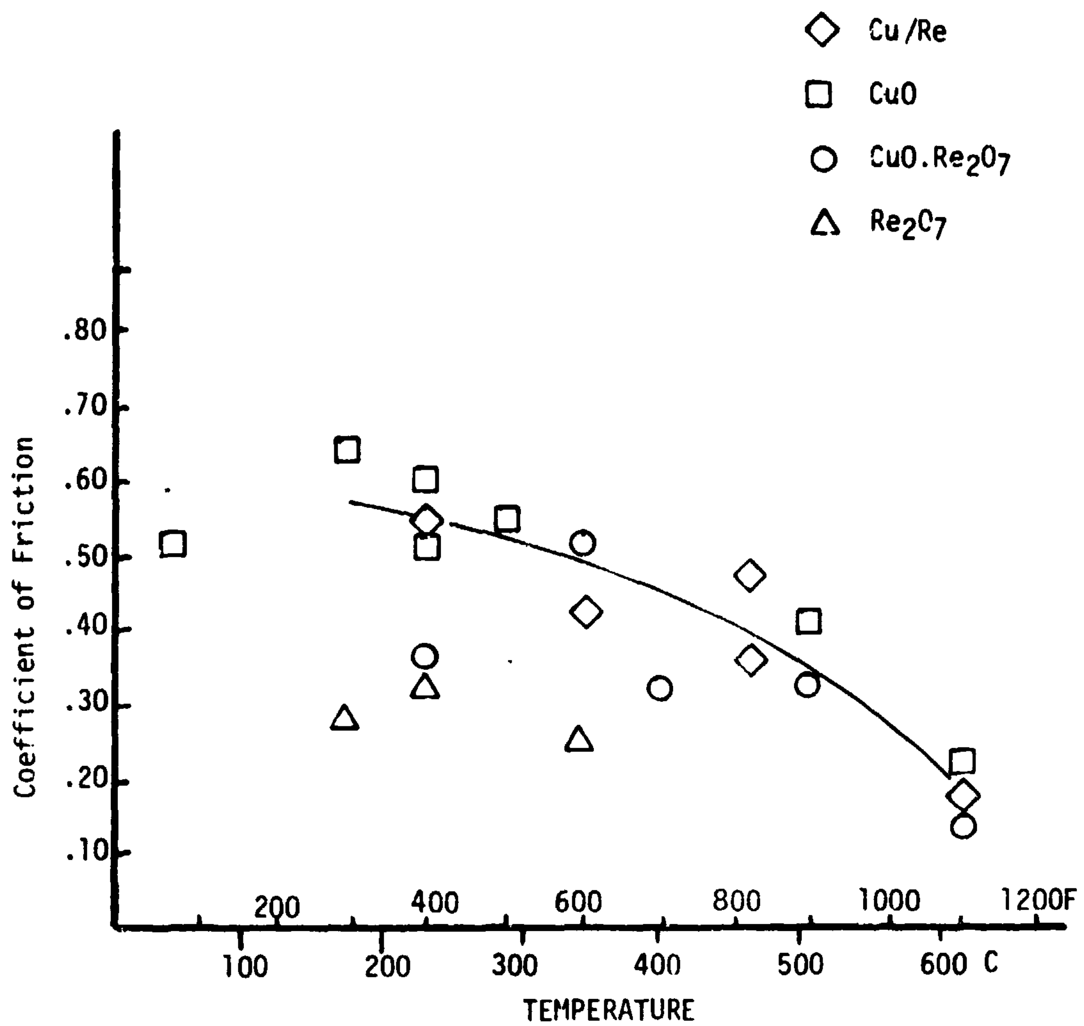

Figure 8. Effect of Temperature on the Coefficient of Friction for Cu/Re Combinations

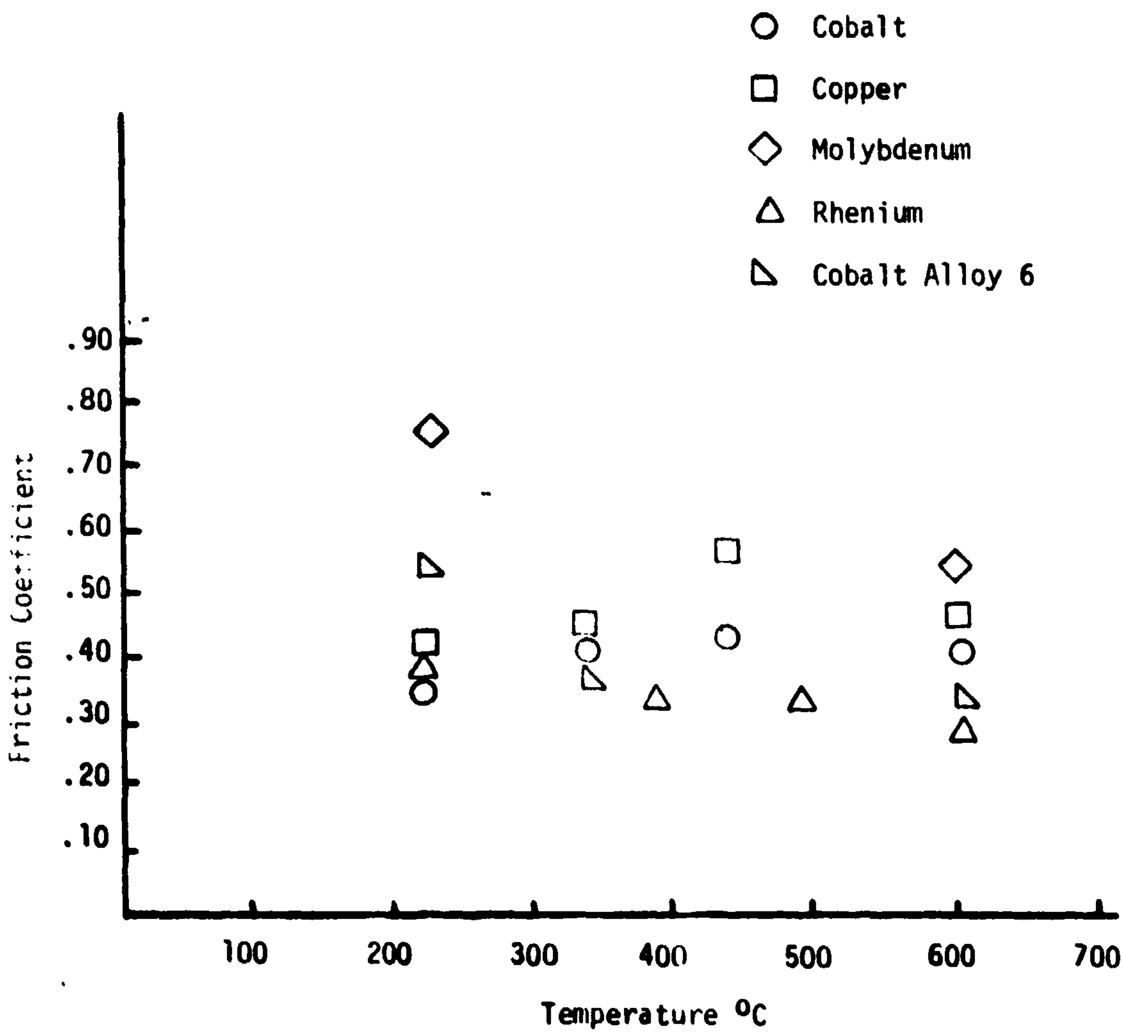

Figure 9. Effect of Temperature on the Friction Coefficient for Metal Powders.

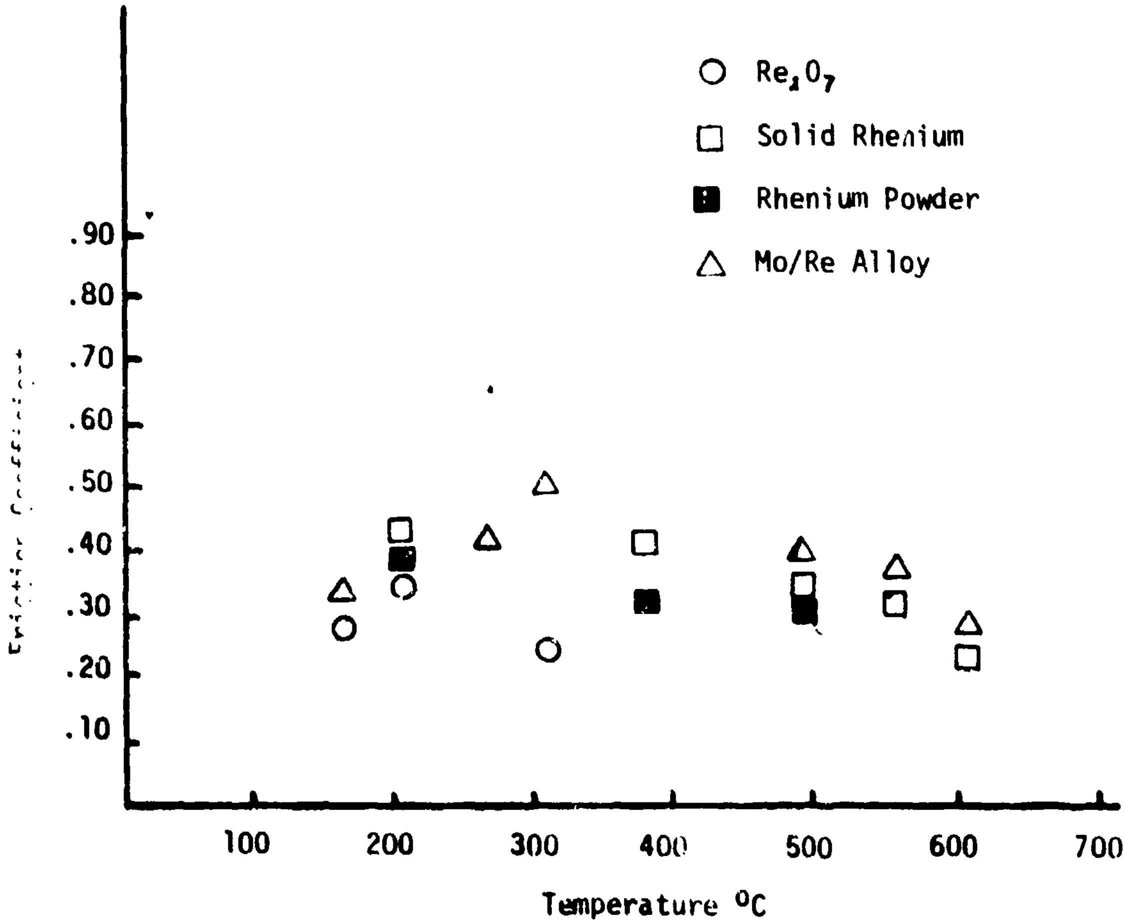

Figure 10. The Effect of Temperature on the Friction Coefficient for Rhenium and Rhenium Alloys.

The data for the 3 to 1 Co/Mo mixture is compared with its various oxides in Figure 11. Friction decreases from 0.41 at 200C to 0.28 at 600C. All of the oxides behave similarly, so it is not possible to define the predominating one; however, the trend is different from either Co or Mo alone (Fig. 9) so it can be assumed one of the oxides is controlling the frictional behavior.

Some interesting results were obtained by comparing Co, Co alloys, and Co oxide as shown in Figure 12. Cobalt powder either on stainless steel or tool steel gave the same frictional behavior as cobalt sliding against cobalt (32). Cobalt alloy #6 powder behaved similarly to the cobalt powder except at room temperature where higher values were obtained. The higher values at room temperature were probably the effect of the tool steel flat. Cobalt oxide on the other hand gives a completely different friction-temperature behavior beginning at 0.80 at room temperature and decreasing to 0.18 at 600C. This result suggests that the cobalt rather than the cobalt oxide dominates the frictional behavior and suggests its use as a high temperature lubricant rather than its oxide.

LUBRICATION/BEARING CONCEPTS

A summary of the frictional behavior of the best oxides from a sliding friction point of view is given in Figure 13. The lowest friction and film forming abilities when both low and high temperatures are considered was found with the following oxides: Re_2O_7, $CuO.Re_2O_7$, and $CuO.MoO_3$. Cobalt oxide gave lower friction at higher temperatures; however, as the metal results show, cobalt oxide is difficult to form at the lower temperatures; cobalt itself however appears to serve as a solid film lubricant. Cobalt and rhenium borate give reasonable frictional behavior at both temperature ranges but a means must be devised to avoid the high friction peak at 425C. The next question to be answered is how to utilize these lubricants in a practical bearing system. This is duscussed in the following paragraphs.

Three potential lubrication concepts are outlined in Table 7. These concepts are based on the proposition that a material can be developed which will have adequate properties to qualify as a bearing material over the temperature range 20-600C and that, in addition, it will oxidize at high temperatures to provide one of the lubricants suggested in the previous paragraph and that this lubricant will provide for a reasonable rate of bearing wear. Since bearings have been operated using solid film lubricants it is reasonable to assume that the approach is feasible; accordingly, the concepts are directed more to methods of spanning the temperature range.

In concept (1) the naturally occurring oxide (e.g. Cu Rhenate) on the bearing material provides adequate high temperature lubrication. Since this double oxide is soft (hardness estimated as 1.5 moh) it may provide adequate protection at low temperatures. Its friction coefficient is 0.37 at 200C; however, it does have good film forming properties. Furthermore, the friction coefficient of films of lead, gold, and silver at room temperature are 0.30, 0.40, and 0.70 respectively (28) and each have been used to

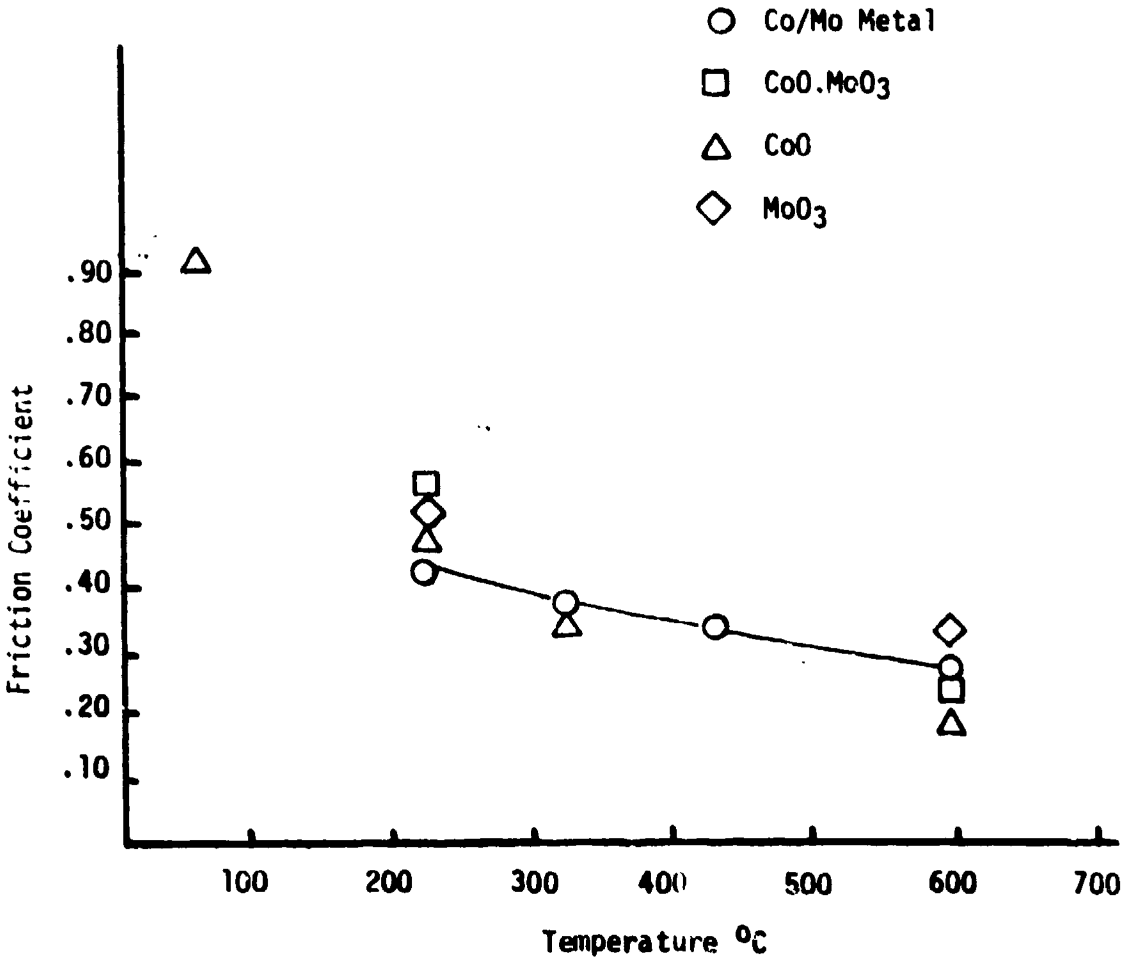

Figure 11. Effect of Temperature on the Friction Coefficient for Cobalt/Molybdenum Combinations

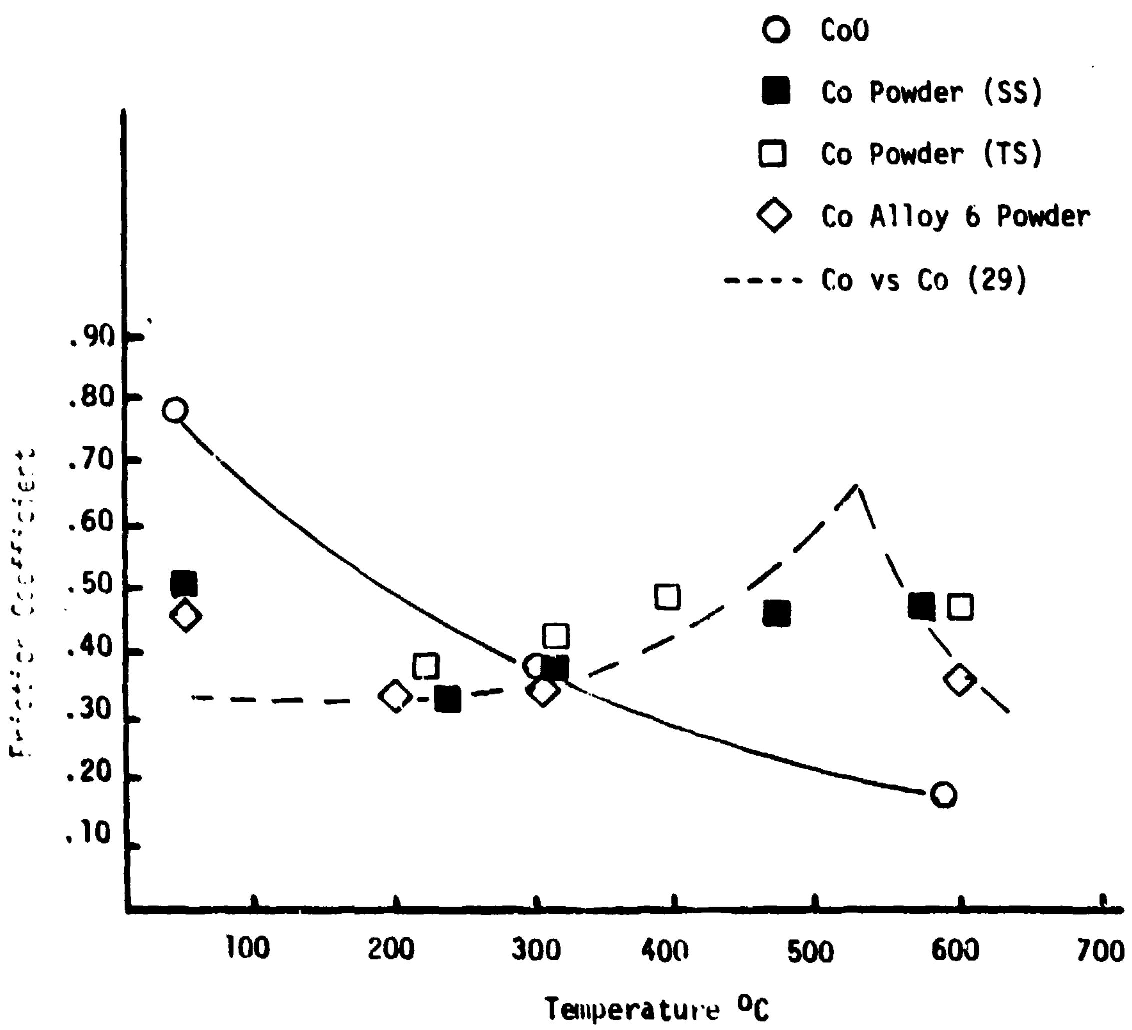

Figure 12. Effect of Temperature on the Coefficient of Friction for Cobalt and Cobalt Alloys

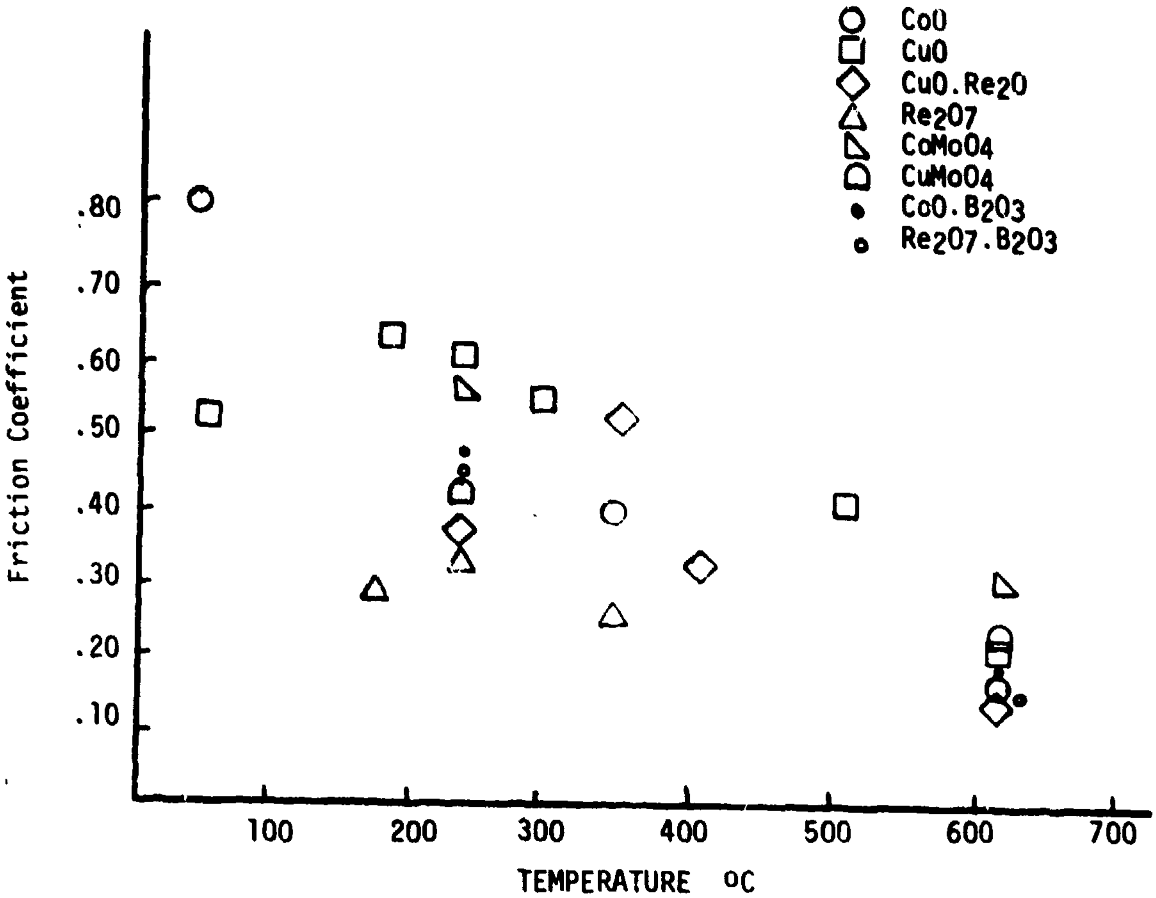

Figure 13. Effect of Temperature on the Friction Coefficient for the Most Effective Oxides.

TABLE 7

LUBRICATION CONCEPTS

(1) The natural occurring oxide on the bearing metal provides effective lubrication at high temperatures. This oxide also gives adequate protection at low temperatures.

(2) The natural occurring oxide on a carbide or boride surface (bonded solid or film) provides effective lubrication at high temperatures. The carbide or boride itself gives adequate protection at low temperatures.

(3) Use either (1) or (2) as a race material combined with a low temperature lubricant (Silver or Cobalt) coated on the ball.

lubricate rolling contact bearings for short periods of time. Whether these naturally occurring oxides are adequate for any given application will have to be determined by experiment.

In concept (2) low temperature operation is not provided by the naturally occurring oxide but by the material itself. For this purpose a ceramic bearing material (boride, carbide, nitride etc.) would be used, since they are able to tolerate some degree of unlubricated operation (33). In this concept the ceramic is used either as a solid or a thin film. This material oxidizes to form a lubricant at high temperatures (Co or Re, oxide or boride) but is capable of operating dry at low temperatures.

Concept (3) provides an additional concept for low temperature lubrication that is a lubricating film of silver or cobalt on the ball. The oxide lubricant would be provided by the race. This approach is suggested by the results of this program. In the original concept it was proposed to add a low temperature lubricant (graphite) to the bearing material; however, in reaction studies at 600C, graphite was found to react with the lubricating oxides, thus a new approach was required. Silver was chosen because it was found to be the only material with low adhesion to B_2O_3 and the borides*. Cobalt was chosen because of the cobalt/cobalt oxide lubrication combination.

There are a variety of ways in which these concepts can be used in practical bearing systems. Materials such as rhenium, copper-rhenium, copper-molybdenum, rhenium boride or cobalt boride could be developed into adequate bearing materials or these same metals could be used as additives in more or less conventional bearing materials. Of these, the latter probably has greater practicality. Although all of the above alloys have been reported in the literature and most are commercially available, an extensive development program would be required before adequate hardness and fatigue resistance could be provided. Small additions in bearing materials, however, may not degrade those properties and reduce development time appreciably. Furthermore, the oxidation rates may be easier to control if oxidizing metals are only an additive in an otherwise oxidization resistant structure.

As an additive, the lubricant producing materials could be introduced into the melt or as an ingredient in the powder metallurgy compact. An even more promising approach may be that of ion-implantation since the additive would not have significant effects on the general material properties and, even more important, could be applied to an already fabricated bearing. Although the depth of penetration is small, the material requirements are small if satisfactory operation is to be obtained. Thus, several different approaches appear to be practical for eventual bearing development.

Unfortunately, both time and financial constraints prevented material developments along these lines and other approaches were required. That

* In this test molten B_2O_3 and the oxide mixtures were heated to 600C while in contact with stainless steel, inconel, tool steel, silver, nickel, and cobalt.

selected was the use of films. Although surface films may not be practical for high DN long life bearings required for turbine engine, they do provide a means for evaluating the concept and reducing the number of variables involved in the material development process.

In order to avoid film development studies it was decided to use either plasma spray or sputtering to apply the films. Because of their availability and applicability to these techniques, two materials were selected (cobalt alloy 6 and B_4C) as the binder for the lubricant producing materials. Additives were Cu/Re, Co/Re, Mo/Re, Cu/Mo, ReB, and CoB_2. As a first step in the evaluation these materials were added to Alloy 6 powder and B_4C powder and evaluated in sliding tests at various temperatures. The results for Alloy 6 are shown in Figure 14. These results are for hardened T15 tool steel sliding against the indicated materials. Cu/Re and Cu/Mo gave the best results with friction coefficients between 0.23 and 0.27 depending upon the temperature. Cu/Re gave a constant value of 0.23 from 200C to 600C. Re/Mo and Re/Co additives gave slightly higher values. Re/Co gave essentially the same values as Alloy 6 at higher temperatures.

The results for B_4C are shown in Figure 15. B_4C without additives gave a constant friction coefficient of 0.41 over the temperature range. None of the additives reduced friction and in fact all gave higher friction values. The reason for this is not clear since PbO in B_4C reduced friction significantly. In any case, the lubricating effect of the oxide was not observed.

THEORETICAL EVALUATION

Previous studies of the wear of films have indicated that they wear in a manner similar (although not at the same rate) to solid materials. In other words, the same equations and general considerations apply. Considering the model of Figure 16, it may be postulated that wear could occur by three mechanisms: flow of material laterally because of repeated load applications; adhesive wear; and fatigue wear or the fracture of the film. Detailed analysis of these mechanisms have not been carried out nor have correlations been attempted between film life and the material properties; however, some insights may be gained by considering the various factors involved. This is attempted in the following sections. The basic problem is to determine what material properties and bearing design parameters would maximize film life.

1. Flow Wear

If a ball in a ball bearing moves against a solid lubricated race (or a solid lubricant coated ball moves against a bare race), the force of the ball against the race will cause solid lubricant to flow out of its way by plastic flow. This will reduce the thickness of the film, but not to zero. A minimum value, a shakedown thickness will exist.

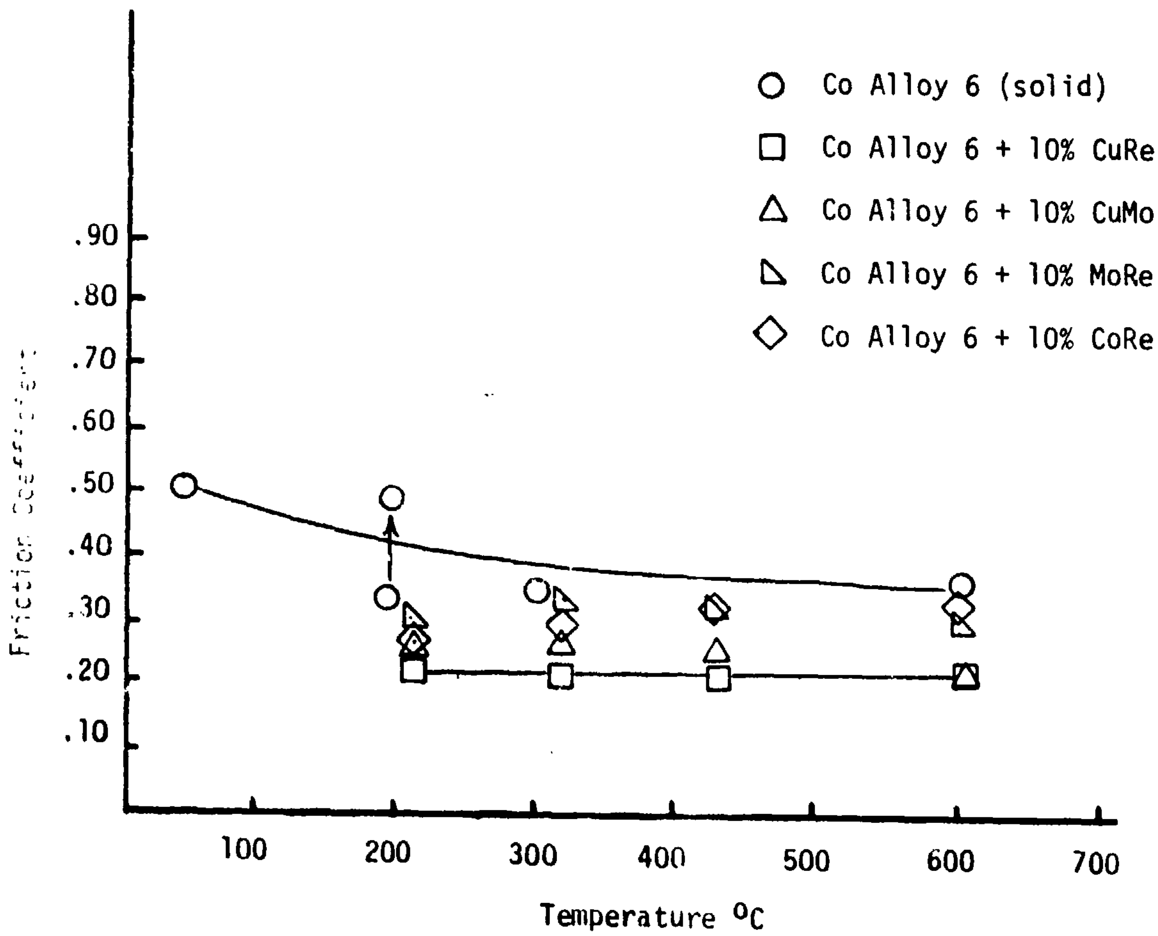

Figure 14. Effect of Temperature on the Coefficient of Friction for Cobalt Alloy 6 Powder Containing Various Additives.

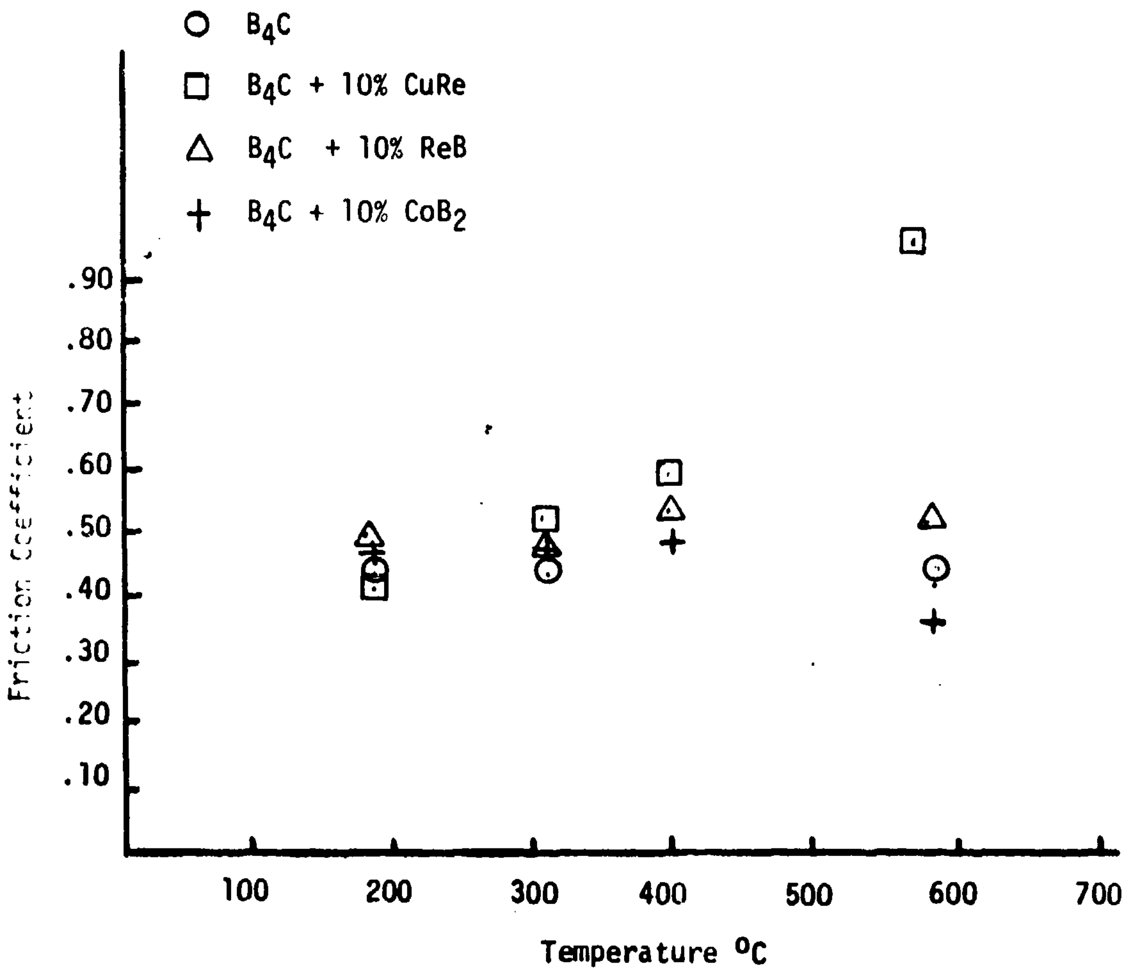

Figure 15. Effect of Temperature on the Coefficient of Friction for B_4C and Additions.

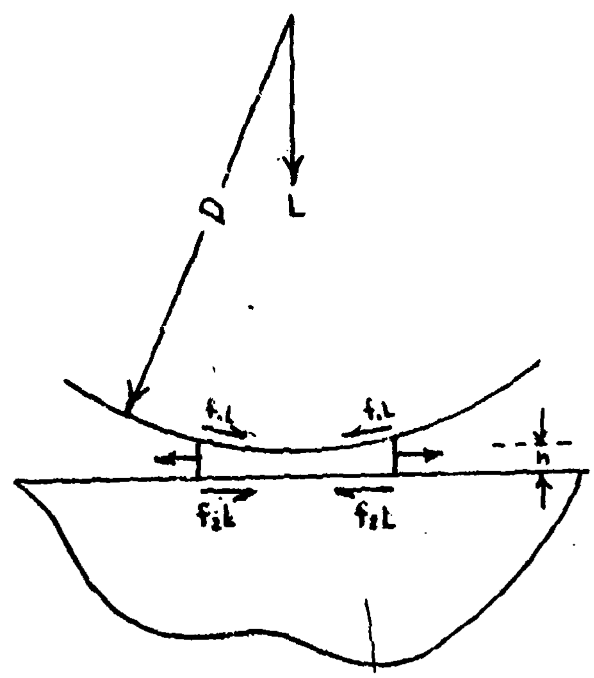

Figure 16. Model for Wear of Soft Lubricating Films

A shakedown thickness exists because of the applied mechanics of film contact. Though the bulk hardness and shear strength of the film will be many times less than that of the ball/race substrate, a virtual stiffening effect occurs due to the nature of plastic flow in a film. Shroeder and Webster (34) showed that the yield strength Y in compression of a cylinder of radius a, depends on the ratio of the radius of the cylinder to its height h, in the following way:

$$\frac{Y}{Y_s} = 1 + 0.385\frac{a}{h} \tag{1}$$

Ys is the bulk shear strength of the cylinder. This effect arises from restraint of outward material motion by adhesive friction forces at both interfaces. Finkin (35) showed that the spherical contact of lead films can be similarly modeled, with a the radius of contact and h the film thickness.

Another film mechanical effect is the increase in shear strength accompanying increasing pressure. In Reference 36 it was shown that:

$$\tau = \tau_0 + \alpha P \tag{2}$$

where τ is the shear strength, τ_0 is the bulk shear strength, p is pressure and α is a constant, which for MoS_2 and graphite is in the range 0.1 - 0.2.

The shakedown thickness is that thickness at which, according to Equation 1, there is a change from plastic to elastic contact.

To maximize the life of the system, high value of shakedown thickness is desired so as to have a lot of material available to be worn by subsequent wear mechanisms.

According to the well known Hertz contact theory, the radius of contact of the ball and the race, ignoring the film, is given by:

$$a = \left(\frac{3}{2} PR \left(\frac{1-\gamma^2}{E}\right)\right)^{1/3} \tag{3}$$

where P is the load on the ball, R is the equivalent radius of a ball on a flat to the ball on the race, γ is Poisson's ratio, and E is the Young's modulus.

From these equations it can be seen that the shakedown thickness can be maximized by having a significant value of yield strength (i.e. greater than 1000 psi), so that the film can benefit from stiffening. As Young's modulus and shear strength/hardness are well known to correlate, this is equivalent to requiring a high value of Young's modulus or hardness. Secondly, high adhesion or friction between the ball and the race would maximize h. Both of these results are contrary to conventional conceptions where low adhesion and low hardness are considered desirable.

The effect of the design parameters can be determined by their effect on the contact radius a. The larger the contact radius, a, the larger is h for a given film. To maximize a requires large diameter balls and close conformance of the ball to the coated race. A smaller number of balls should also be desirable. This will increase the load per ball and bring in the strengthening effect of Equation 2.

2. Adhesive Wear

For whatever solid film lubricant shakedown thickness exists, the adhesive wear rate should be as low as possible without a transition occurring to a catastrophic wear mechanism (e.g., film fatigue, subsurface spalling). This will be affected by both materials and design parameters.

The well known linear wear equation which models this situation is:

$$V = \frac{KPL}{H} \tag{4}$$

where V is the wear volume, P is the load, H is the hardness of the substrates and L is the sliding distance. K is then the dimensionless wear coefficient. For film covered ball bearing contact, wear life is limited by film thickness h so:

$$h = \frac{V}{A} = \frac{K}{A}\frac{PL}{H} = \frac{KPL}{\pi \beta H D d} \tag{5}$$

where A is the area of the film, given by:

$$A = \beta \pi D d \tag{6}$$

where D is the bearing outer race diameter, d is the ball diameter and β is a geometric coefficient.

The wear life of the film is goverened by Equation 5 which contains both materials and design parameters:

$$L = \frac{h \pi \beta H D d}{KP} \tag{7}$$

Minimizing sliding distance required minimizing the microslip/revolution. Reference 37 graphically relates all major ball bearing geometric factors to microslip per revolution. This is shown in Figure 17. It was found that to accomplish this we need to maximize the value of:

$$C = f_c \, (i \, \cos\alpha)^{0.7} Z^{2/3} d^{1.8} \tag{8}$$

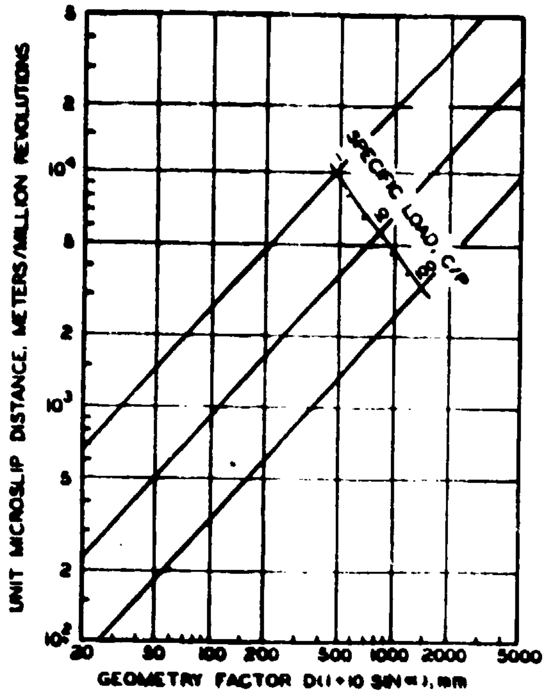

Figure 17. Approximate Microslip in Rolling Contact Bearings (Silbey 37)

where f_c is a geometric constant, L is the number of rows of balls or rollers, α is the contact angle, Z is the number of balls,row, d is the ball diameter and D is the bearing outer diameter.

It was also shown that microslip increases with the quantity D ($1 + 10 \sin \alpha$) raised to a power of less than one, say typically 0.38. Combining this finding with Equation 5 which has D in the denominator implies that bearing diameter per se has little influence on wear life.

In view of Equations 7 and 8 the significant parameters for the maximum film life can be defined for adhesive type wear. The main material parameters are the hardness of the film and K the dimensionless wear coefficient. Higher hardness and lower K mean lower wear rates and thus longer life for a given film thickness, h. A review of the factors affecting K (38) show that low K is characteristic of non-soluble or non-reactive couples. Hexagonal structures and low ductility also reduce K. An example of this would be noble metal such as silver in contact with an oxidized surface. It is difficult to combine all of these factors into a given material but high hardness and low friction between the ball material and surface film would seem to be a good criteria, where friction is taken as a measure of the adhesive interaction. The design parameters which would extend film life are large diameter balls, use of a large number of balls (weak effect) and the use of close conformity balls and race to increase β and the wearing area.

These results show that both flow wear and adhesive wear reduction require higher hardness, large diameter balls, and close ball/race conformity. The most significant result is that of hardness since it implies that some materials which might not be expected to perform well may be satisfactory and, in fact, better in rolling contacts than very soft films like MoS_2. This, of course, is based on the presumption that flow wear and adhesive wear are the correct wear mechanisms.

There is, of course, a limit to the beneficial effects of hardness. That limit would be the fracture toughness or fatigue properties. Harder films would be brittle and wear by fatigue or fracture mechanisms. Thus, some film ductility is needed but it is difficult to define actual values required. This should be determined experimentally.

It is of value to estimate the life of bearings lubricated with solid films to determine the theoretical feasibility of this approach. The approach used was that of Sibley (39) which in essence calculated the microslip in a bearing and uses this as the sliding distance in the wear Equation (5). A typical turbine engine bearing was used under the following conditions:

Bore	1.18 in (30 mm)	Contact Angle	18.6°
O.D.	1.85 in (47 mm)	Radius	53°
Width	.35 in (9 mm)	Material	Steel
Load	98 lbs (444N)	Ball No.	17
Speed	63,500 RPM	Life	25 hours
Ball Dia.	.219 in (5.56 mm)	Pitch	1.52" (38.5 mm)

The microslip is determined to be 14.3 x 10^4 meters (5.63 x 10^6 in) using Figure 17 and the following equations:

$$C = f_c\,(i\cos\alpha)^{.7} Z^{2/3} D_w^{1.8}$$

$$\frac{D_w \cos\alpha}{d_m} = 0.14$$

$$f_c = 58.5 \text{ (Ref 37 TABLE 2)}$$

$$\frac{C}{P} = 10.43$$

$$D = 1410 \sin\alpha = 197$$

C = Load capacity
P = Load
f_c = Load capacity factor
α = Contact angle
Z = No. of balls
Dw = Ball diameter
dm = Pitch diameter
D = O.D.

Transforming the wear equation:

$$h = \frac{K}{H}\,\frac{LS}{A}$$

K = Dimensionless wear coef.
H = Hardness kg/mm^2
L = Load N
A = Area mm^2
S = Microslip mm

Using this equation with the previous bearing parameters and moh hardness values typical of the oxide films being proposed as lubricants, the depth of wear, h, is plotted against the hardness for various wear coefficients in Figure 18. This graph shows the amount of wear after 25 hours of bearing operation. In other words, a film thickness, h, must be applied to get 25 hours life. If the film properties were better defined a second curve based on flow wear could be added which would give the starting h = hi. For a given wear coefficient then hi must be greater than h from Figure 18 or the bearing would not last 25 hours.

Even without this data certain conclusions can be drawn. Applied film thickness of solid film lubricants are generally in the range of .003 to .015 mm so this would be a reasonable value for hi. With this value of hi and hardness values of moh 1 to 3 it can be seen that wear coefficients of 10^{-8} will be required. These are extremely low values, more typical of boundary lubrication. Solid film lubricants (without reapplication techniques) usually have values of 10^{-6} to 10^{-7} at best. This does not mean that the task is impossible since the naturally occurring oxide is reformed as it is worn away. It does mean, however, that it must be reformed at a rate of approximately .2 mil/25 hours to compensate for this loss and hold bearing dimensions.

Further efforts require actual wear coefficients from bearing tests. When these are obtained it is possible to determine how changes in bearing parameters, operating conditions, and film properties will affect the ultimate bearing life.

BEARING EVALUATION

In order to effectively evaluate the concept of bearing lubrication at high temperature it would be necessary to use one of the following approaches:

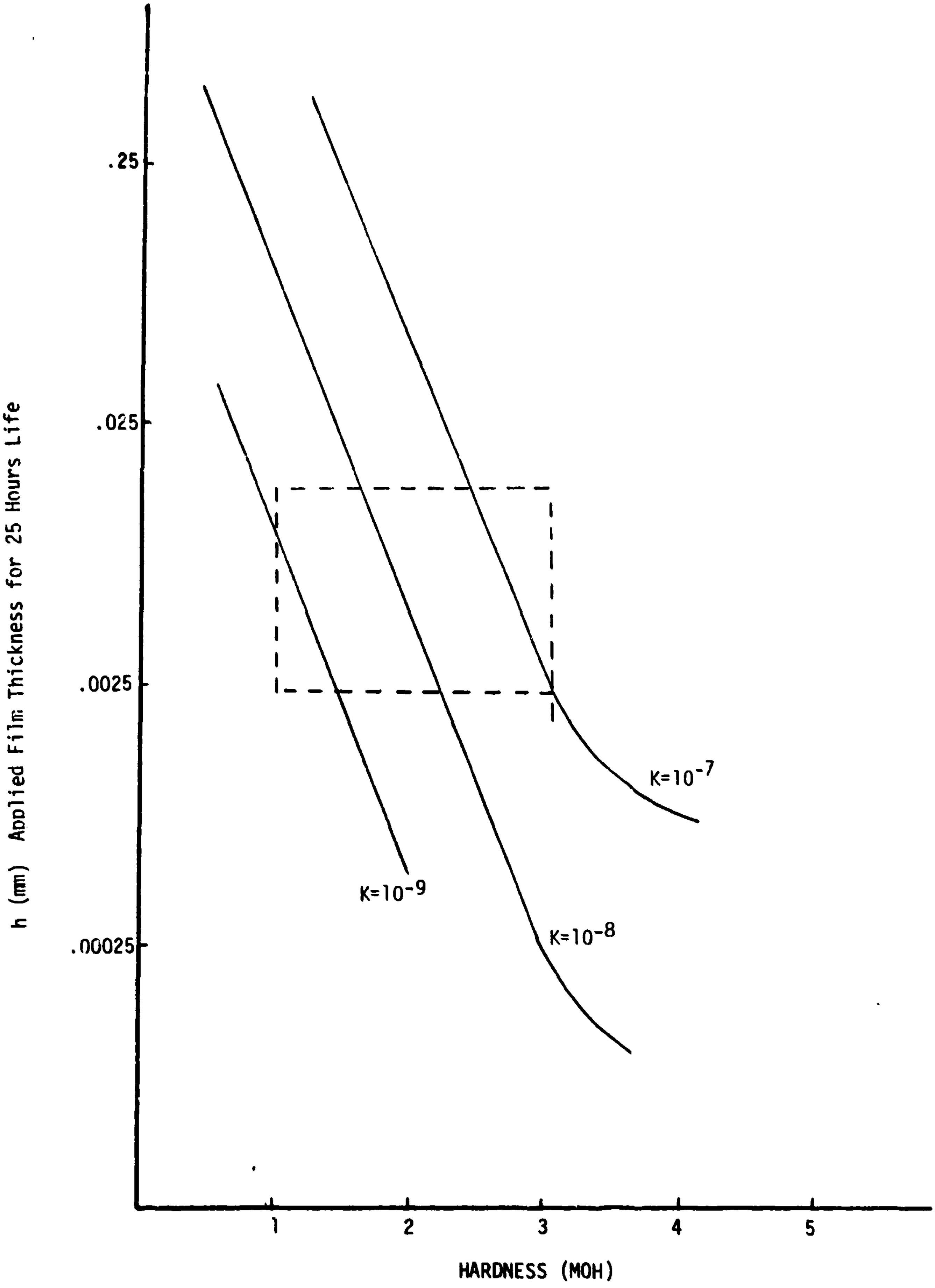

Figure 18. Wear Rates for Rolling Contact Bearings

(1) Fabricate bearings of a cobalt base alloy or ceramic which would contain additives of copper and rhenium or copper and molybdenum. (2) Fabricate bearings of cobalt base alloys or ceramics and implant ions of copper, rhenium, molybdenum, or boron or (3) Purchase bearings of high temperature materials and coat them with a film of lubricant producing materials. The first two approaches would require considerable development work just to reach the bearing producing stage. Approach (3) has limitations because of the availability of high temperature ball and race materials. Thus considerable comprises were necessary in the bearing evaluation. However, through the courtesy of M. Gardos of Hughes Aircraft and the DARPA Solid Lubricated Rolling Element Bearing Program several bearings were obtained. In addition, some rolling ball tests were conducted using available high temperature materials. These are described in the following paragraphs.

As a preliminary test of the concept, rolling ball tests were conducted with a cobalt bonded titanium carbide ball (1.17in. or .500 in. dia) and a sand blasted 304 stainless steel flat. Powders of Cu/Re (50/50 by weight) and Cu/Mo (66/33 by weight) were placed on the surface to fill the roughness. Tests were run for 1½ hours, 142N (32 lbs) load at a temperature of 600C (1100F). The results of the tests are shown in Table 8. Although friction coefficients were higher for Cu/Re, all friction coefficients were low. However, the most significant result was that, as would be expected, there was metal transfer and damage with the stainless steel and no damage with the metal powder surface coating. Thus a poor material combination was effectively lubricated. Efforts were then directed into more practical evaluations.

Rolling ball tests were conducted under the same conditions as the previous tests using plasma sprayed films of cobalt alloy 6 containing lubricant producing metal powders and sputtered carbide films. Ten percent additions were used, five percent per element. Detail of film applications are given in Table 9. The results of these tests are given in Table 10. The friction coefficients were low for the Cu/Re and the Cu/Mo and remained constant throughout the test. There was very little surface damage in the track although there was a groove about as deep as the film thickness. There were material voids in the track. These were undoubtedly due to the porosity of the film which was about 15 percent. There was no evidence of [illegible] contact through the film. A cross section of the Cu/Re film showed that the original film in the track area was about 0.02 cn thick and the final film was 0.009 cn thick. How much of this was wear and how much was compression could not be determined; however, very little wear debris was produced. Microscopic examination of the track showed that about 50 percent of the track consisted of oxide colored polished areas while the remainder appeared to be spalled areas where particles had been removed.

With rhenium alone there was an increase in friction during the course of the test and evidence of film breakup in the track. With the stainless steel alone there was considerable transfer from the ball to the flat which built up a thick rough film on the stainless steel. Film spalling was found for the Cr_2O_3 which might be expected due to the high pressures involved with the high ball loads.

Bearing tests were also run using the alloy 6/metal additive films with about the same results as the rolling ball tests. The bearings were GT-7 full complement ball (12 balls) thrust bearings (O.D. 47 mm; I.D. 22 mm). The materials proposed for use are listed in Table 11. They are organized to evaluate the three lubrication concepts proposed in Table 7. Actually all of the race coatings were not evaluated because they could not be procured; primary emphasis was given to the alloy 6/additive coatings. The actual coatings applied to the stainless steel races are described in Table 9.

The results for the bearing tests are shown in Table 12 along with the procedure. The tests were run at light loads to avoid film spalling; the velocity was 300 RPM. They were first run in with cetane to form a track. Tests were then run at 400C. After running at 400C for one hour the test was stopped and the bearings were inspected. For the metal additives the wear was approximately .02 mm after 1 hour. Although this is not a great deal of wear, inspection of the races indicated the same condition as that found for the rolling ball tests. Part of the track area consisted of polished oxide coated surfaces; other areas appeared to be spalled and this spalled debris was randomly distributed over the polished surface.

TABLE 8

ROLLING BALL TESTS WITH METAL POWDERS

TiC Ball vs Stainless Flat; 142N; 600C; 1½ hrs; 1 cy/sec

Powder	Friction Coefficient	Surface Damage
None	.046	Rough surface on flat. Material transferred to ball.
Cu/Re	.093	Indented surface with no damage. Thin polished coating on ball
Cu/Mo	.046	Indented surface with some transfer. Polished film on ball

TABLE 9

BEARING RACE COATINGS

Coating	Label	Substrate Thickness	Substrate and Bond Coat Thickness	Bond Coat Thickness	Final Thickness	Coating Thickness	Recommended Grind to Dimension
Co Alloy6	A1	.1886	.1891	.0005	.2010	.012	.196-.197
10% Re	A2	.1890	.1907	.0007	.2020	.011	.196-.197
Co Alloy6	B1	.1887	.1910	.0023	.2030	.012	.196-.197
5% Cu	B2	.1890	.1906	.0016	.2040	.013	.196-.197
5% Re							
Co Alloy6	C1	.1874	.1885	.0011	.2020	.013	.196-.197
5% Cu	C2	.1881	.1894	.0013	.2010	.012	.196-.197
5% Mo							
Boron	D1	.1888	.1916	.0028	NA		NA
Carbide	D2	.1881	.1895	.0014	NA		NA
Chromium	E1	.188	.190	.002	.201	.011	.196-.197
Oxide	E2	.188	.190	.002	.202	.012	.196-.197
Sputtered						12000A	NA
Boron						12000A	NA
Carbide							

TEST PANELS FOR SLIDING FRICTION

After grit blast dimension 0.253 to 0.254"
After bond coat dimension 0.255 to 0.256"
Bond coat thickness 0.002"

Coating	Label	Finish Dimension	Grind to Dimension
Co Alloy 6	A	.268	
10% Re		.267	.262-.263"
Co Alloy 6	B	.272	.262-.263"
5% Cu		.271	
5% Re			
Co Alloy 6	C	.269	.262-.263"
5% Cu		.268	
5% Mo			
Boron Carbide	D	NA	NA
Chromium	E	.275	.262-.263"
Oxide		.270	
Sputtered Boron Carbide	NA	12000 Angstroms	NA

TABLE 10

ROLLING BALL TESTS - COATED SURFACES

Cobalt Alloy J Balls vs 304 Stainless Steel Flat
Temp 650C; Load 142N; Velocity 1 cy/sec; 14 hours

Coating	f_i	f_f	Surface Damage
None	.040	.046	Thick rough buildup on stainless steel from ball transfer
Co Alloy6/10 CURe	.014	.014	Track groove (.013 cn deep) Smooth surface with isolated voids. Oxide film on track surface and ball
Co Alloy 6/10 CuMo	.014	.014	Track Groove (.013 cn deep) Smooth surface with isolated voids. Oxide film on track surface and ball.
Co Alloy6/10 Re	.014	.022	Roughened track with loose debris
Cr_2O_3	.022		Spalling in track, loose powder

TABLE 11

MATERIALS SELECTED FOR BEARING TESTS

	Concept 1	Concept 2	Concept 3
Upper Race	304 SS	304 SS	304 SS
Race Coating	Co Alloy 6/Re*	B_4C**	B_4C**
	Co Alloy 6/Cu/Re*	B_4C/Co_2B**	Co Alloy 6/cu/Re*
	Co Alloy 6/Cu/Mo*	Co_2B**	
		Cr_2O_3*	
Ball	Co Alloy J	Co Alloy J	Co Alloy J
Ball Coating	None	None	Ag**
			Co**
Lower Race	T 15 Tool Steel	T 15 Tool Steel	T 15 Tool Steel

* Plasma spray.
** Sputtered

TABLE 12

THRUST BEARING TESTS

Stack Height mm

	Cu/Re	Cu/Mo	Re	Cr_2O_3	B_4C
As supplied	16.09	16.06	16.00	16.05	15.90
After 1 hr with Headecane lube 3.5 Kg load	16.09	16.06	16.00	16.04	15.90
After 1 hr at 400c; 12 Kg load	16.07	16.04	15.97	15.99	15.88

CONCLUSIONS AND RECOMMENDATIONS

1. Certain oxides and double oxides are effective lubricants over the temperature range 200-650C. These are cobalt oxide, copper oxide, copper rhenates, rhenium oxide, cobalt molybdate, copper molybdate, cobalt borate, and rhenium borate. These compounds prevent surface damage in rolling and sliding contacts and yield friction coefficients which vary from 0.30 to 0.60 at 200C to 0.14 to 0.32 at 650C. These oxides could be used as naturally occurring lubricants on high temperature alloys.

2. Metal alloys and mixed metal powders containing rhenium, copper/rhenium, molybdenum/rhenium, cobalt/molybdenum and copper/molybdenum yielded frictional behavior similar to the expected double oxide. When these lubricant producing metals were added to a cobalt base alloy powder, friction was reduced from 0.35 to 0.21 over the temperature range 200C to 650C.

3. A wear analysis of a typical rolling contact bearing operating at 63,500 RPM at a load of 444N(98 lbs) indicates that wear coefficients of 10^{-7} or 10^{-8} will be required for 25 hours life. These are lower values than are generally found for unreplenished solid films; however, they would be feasible if oxidation rates were sufficient to replenish the film.

4. Based upon theoretical considerations, it is proposed that wear of films occurs by plastic flow, adhesion, and fracture. Plastic flow takes place initially to establish a critical film thickness; thereafter, wear takes place by adhesive processes, while new film is formed by oxidation. The lubricating film should be as hard as possible without fracture; thus, fracture toughness appears to be the most significant property for long wear life. Design parameters of significance for long life are large diameter balls and close ball/race conformity.

5. Rolling ball tests and bearing tests were conducted using plasma sprayed cobalt alloy 6 containing 10 percent additions of Re, Cu/Re, and Cu/Mo. Wear coefficients (10^{-3}-10^{-4}) were much higher than those required (10^{-7}-10^{-8}) for 25 hours life. Microscopic observations showed that this was due to break up of the alloy 6 film under the high stresses rather than a lubrication failure. Further tests are needed with more durable films.

6. Further bearing testing is recommended using denser, better defined materials. Three approaches are recommended: (1) Hot isostatic pressed cobalt and nickel containing alloys containing additions of rhenium, copper, molybdenum, and boron, (2) Ion implantation of atoms of rhenium, copper, cobalt and molybdenum, and (3) Sputtering films of mixed borides on metal and nitride bearings.

7. A further analysis of film wear processes is recommended. Specifically, wear rates in rolling contacts using films of known properties are needed. Using these data a more comprehensive analysis of lubricating film wear can be developed which includes flow wear, adhesive wear, and fracture wear.

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